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16. ABSTRACT

The Exposure Analysis Modeling System (EXAMS) was designed for rapid evaluation of the behavior of synthetic organic chemicals in aquatic ecosystems. From the chemistry of a compound and the relevant transport and physical/chemical characteristics of the ecosystem, EXAMS computes:

1. Exposure: the ultimate (steady-state) expected environmental concentrations (EECs) resulting from a specified pattern of (long-term, time-invariant) chemical loadings,
2. Fate: the distribution of the chemical in the system and the fraction of the loadings consumed by each transport and transformation process, and
3. Persistence: the time required for effective purification of the system (via export/transformation processes) once the chemical loadings cease.

EXAMS conbines loadings, transport, and transformations into a set of differential equations using the law of conservation of mass as an accounting principal. This law accounts for all of the chemical mass entering and leaving a system as the algebraic soum of external loadings, transport processes that export the compound from the system, and transformation processes that convert the parent compound to daughter products.

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EXPOSURE ANALYSIS MODELING SYSTEM (EXAMS):

User Manual and System Documentation

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FOREWORD

Environmental protection efforts are increasingly directed toward preventing adverse health and ecological effects associated with specific compounds of natural or human origin. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Environmental Systems Branch studies complexes of environmental processes that control the transport, transformation, degradation, fate, and impact of pollutants or other materials in soil and water and develops models for assessing exposures to chemical contaminants.

Concern about environmental exposure to synthetic organic compounds has increased the need for techniques to predict the behavior of chemicals entering the environment as a result of the manufacture, use, and disposal of commercial products. The EXposure Analysis Modeling System (EXAMS), which has been under development at this Laboratory for more than 3 years, provides a convenient tool to aid in judging the environmental consequences should a specific chemical contaminant enter a natural aquatic system. Because EXAMS requires no chemical monitoring data, it can be used for new chemicals not yet introduced into commerce as well as for those whose record of use is known. EXAMS and other exposure assessment models should contribute significantly to efforts to anticipate potential problems associated with environmental pollutants.

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ABSTRACT

The EXposure Analysis Modeling System (EXAMS) was designed for rapid evaluation of the behavior of synthetic organic chemicals in aquatic ecosystems. From the chemistry of a compound, and the relevant transport and physical/chemical characteristics of the ecosystem, EXAMS computes:

1) Exposure: the ultimate (steady-state) expected environmental concentrations (EECs) resulting from a specified pattern of (long term, time-invariant) chemical loadings,
2) Fate: the distribution of the chemical in the system and the fraction of the loadings consumed by each transport and transformation process, and
3) Persistence: the time required for effective purification of the system (via export/transformation processes) once the chemical loadings terminate.

EXAMS is an interactive program; it allows a user to specify and store the properties of chemicals and ecosystems, modify the characteristics of either via simple English-like commands, and conduct efficient, rapid evaluations and sensitivity analyses of the probable aquatic fate of synthetic organic chemicals.

EXAMS combines loadings, transport, and transformations into a set of differential equations by using the law of conservation of mass as an accounting principle. This law accounts for all the chemical mass entering and leaving a system as the algebraic sum of (1) external loadings, (2) transport processes that export the compound from the system, and (3) transformation processes that convert the parent compound to daughter products. EXAMS' fundamental equations describe the rate of change of chemical concentrations as a balance between increases originating from external and internally recycled loadings, and decreases resulting from transport and transformations. The set of unit process models that compute the dynamic behavior of a compound is the central core of EXAMS. These are all "system-independent" models, that is, each formulation includes a direct statement of the interactions between the chemistry of a compound and the environmental forces that shape its behavior in aquatic systems.

EXAMS' environmental data are contained in a file composed of concise descriptions of the aquatic systems of interest to a user. Each water body is represented via a set of N compartments or distinct zones in the system. EXAMS has been designed to accept standard water-quality and limnological parameters. EXAMS also includes a descriptor language for specification of system geometry and connectedness. The code has been written in a general (N-compartment) form. The software is available in 10-, 50-, or 100-compartment versions. The code will support larger versions, up to a limit of 999 environmental compartments.

This report covers a period from June 1, 1978 to January 30, 1981 and work was completed as of January 30, 1981.

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The system-independent process models used in EXAMS are its central core. We were critically dependent upon cooperation and advice provided by specialists in the environmental chemistry of transformation and sorption processes. We are particularly grateful to G.L. Baughman, D.S. Brown, S.W. Karickhoff, D.F. Paris, W.C. Steen, N.L. Wolfe, and R.G. Zepp for fruitful discussions and reviews of EXAMS.

EXAMS was originally released for testing in October of 1979. A number of users have detected "bugs" in the program and advised us of their findings. Assuredly additional problems will surface as EXAMS receives wider usage; we are always grateful for any information that can be used to improve the program.

The discussion of EXAMS' batch input data (Section 3.4) was prepared by Felice O. Burchfield.

We are grateful to Bruce Bartell, Steven Hodge, Ronnie Moon, and Caroline Phillips for their assistance in preparing the illustrations and typescript of this report.

SECTION 1

INTRODUCTION

1.1 Background

Industrial production of agricultural chemicals, plastics, and pharmaceuticals has steadily increased over the past three decades. More recently, growth of the chemical industry has been accompanied by increasing concern over the effects of synthetic chemicals on the environment. The suspicion has arisen that, in some cases, the benefits gained by using a chemical may not offset the cost of incidental damage to man's natural life-support systems. The toxicity of a chemical does not of itself indicate that the environmental risks associated with its use are unacceptable, however. A rational evaluation of the risk posed by the use and disposal of synthetic chemicals must begin from a knowledge of the exposure, persistence, and fate of chemicals in the environment.

The EXposure Analysis Modeling System (EXAMS), developed at the Athens Environmental Research Laboratory, is an interactive computer program intended to give decision-makers in industry and government access to a responsive, general, and controllable tool for readily deriving and evaluating the behavior of synthetic chemicals in the environment. Initial work has focused on the development of the interactive command language and user aids that are the core of EXAMS, and on the genesis of the first EXAMS mathematical model. This model was designed primarily for the rapid screening and identification of synthetic organic chemicals likely to adversely impact aquatic systems. This report is intended to acquaint potential users with the underlying theory, capabilities, and use of the system.

1.2 Exposure Analysis in Aquatic Systems

EXAMS was conceived as an aid to those who must execute hazard evaluations solely from laboratory descriptions of the chemistry of a newly synthesized toxic compound. EXAMS estimates exposure, fate, and persistence following release of an organic chemical into an aquatic ecosystem. Each of these terms was given a formal operational definition during the initial design of the system.

1.2.1 Exposure

When a pollutant is released into an aquatic ecosystem, it is entrained in the transport field of the system and begins to spread to locations beyond the original point of release. During the course of these movements, chemical and biological processes transform the parent compound into daughter products. In the face of continuing emissions, the receiving system evolves toward a "steady-state" condition. At steady state, the pollutant concentrations are in a dynamic equilibrium in which the loadings are balanced by the transport and transformation processes. These residuals can be compared to the concentrations posing a danger to living organisms. The comparison is one indication of the risk entailed by the presence of a chemical in natural systems or in drinking-water supplies. These "expected environmental concentrations" (EECs), or exposure levels, in receiving water bodies are one component of a hazard evaluation.

1.2.2 Persistence

Toxicological and ecological "effects" studies are of two kinds: investigations of short-term "acute" exposures, as opposed to longer-term "chronic" experiments. Acute studies are often used to determine the concentration of a chemical resulting in 50% mortality of a test population over a period of hours. Chronic studies examine sub-lethal effects on populations exposed to lower concentrations over extended periods. Thus, for example, an EEC that is 10 times less than the acute level does not affirm that aquatic ecosystems will not be affected, because the probability of a "chronic" impact increases with exposure duration. A computed EEC thus must be supplemented with an estimate of "persistence" in the environment. (A compound immune to all transformation processes is by definition "persistent" in a global sense, but even in this case transport processes will eventually reduce the pollutant to negligible levels should the input loadings cease.) The notion of "persistence" can be given an explicit definition in the context of a particular contaminated ecosystem: should the pollutant loadings cease, what time span would be required for dissipation of most of the residual contamination? (For example, given the half-life of a chemical in a first-order system, the time required to reduce the chemical concentration to any specified fraction of its initial value can be easily computed.) With this information in hand, the appropriate duration and pollutant levels for chronic studies can be more readily decided.

1.2.3 Fate

The toxicologist also needs to know which populations in the system are "at risk." These can to some extent be deduced from the distribution or "fate" of the compound, that is, by an estimate of EECs in different sectors of the ecosystem. EXAMS reports a separate EEC for each compartment, and each local population, used to define the system.

The concept of the "fate" of a chemical in an aquatic system has an additional, equally significant meaning. Each transport or transformation process accounts for only part of the total behavior of the pollutant. The relative importance of each process can be determined from the percentage of the total system loadings consumed by the process. The relative importances of the transformations indicate which process is dominant in the system, and thus in greatest need of accuracy and precision in its kinetic parameters. Overall dominance by transport processes may imply a contamination of downstream systems, loss of significant amounts of the pollutant to the atmosphere, or pollution of ground-water aquifers.

1.3 THE EXAMS Program

The need to predict chemical exposures from limited data has stimulated a variety of recent advances in environmental modeling. These advances fall into three general categories:

1. Process models giving a quantitative, often theoretical, basis for predicting the rate of transport and transformation processes as a function of environmental variables.

2. Procedures for estimating the chemical parameters required by process models. Examples include linear free energy relationships, and correlations summarizing large bodies of experimental chemical data.

3. Systems models that combine unit process models with descriptions of the environmental forces determining the strength and speed of these processes in real ecosystems.

The vocabulary used to describe environmental models includes many terms, most of which reflect the underlying intentions of the modelers. Models may be predictive, stochastic, empirical, mechanistic, theoretical, deterministic, explanatory, conceptual, causal, descriptive, etc. The EXAMS program is a deterministic, predictive systems model, based on a core of mechanistic process equations derived from fundamental theoretical concepts. The EXAMS computer code also includes descriptive empirical correlations that ease the user's burden of parameter calculations, and an interactive command language that facilitates the application of the system to specific problems.

EXAMS "predicts" in a somewhat limited sense of the term. Many of the predictive water-quality models currently in use include site-specific parameters that can only be found via field calibrations. After "validation" of the model by comparison of its calibrated outputs with additional field measurements, these models are often used to explore the merits of alternative management plans. EXAMS, however, deals with an entirely different class of problem. Because newly synthesized chemicals must be evaluated, little or no field data may exist. Furthermore, EECs at any particular site are of little direct interest. In this case, the goal, at least in principle, is to predict EECs for a wide range of ecosystems under a variety of geographic, morphometric, and ecological conditions. EXAMS includes no direct calibration parameters, and its input environmental data can be developed from a variety of sources. For example, input data can be synthesized from an analysis of the outputs of hydrodynamic models, from prior field investigations conducted without reference to toxic chemicals, or from the appropriate limnological literature. The EECs generated by EXAMS are thus "evaluative" (Lassiter, Baughman, and Burns 1978) predictions designed to reflect typical or average conditions. EXAMS' environmental data base can be used to describe specific locales, or as a generalized description of the properties of aquatic systems in broad geographic regions.

EXAMS relies on mechanistic, rather than empirical, constructs for its core process equations. Mechanistic (physically determinate) models are more robust predictors than are purely empirical models, which cannot safely be extended beyond the range of prior observations. EXAMS contains a few empirical correlations among chemical parameters, but these are not invoked unless the user approves. For example, the partition coefficient of the compound on the sediment phases of the system, as a function of the organic carbon content of its sediments, can be estimated from the compound's octanol-water partition coefficient. A direct load of the partition coefficient (KOCG, see Glossary) overrides the empirical default estimate, however.

(Because EXAMS is an interactive program in which the user has direct access to the input data base, much of this documentation has been written using the computer variables (e.g., KOCG above) as identifiers and as quantities in the process equations. Although this approach poses some difficulties for the casual reader, it allows the potential user of the program to see the connenctions between program variables and the underlying process theory. The Glossary section of this document includes an alphabetical listing and definitions of EXAMS' input variables.)

EXAMS is a deterministic, rather than a stochastic, model in the sense that a given set of inputs will always produce the same output. Uncontrolled variation is present both in ecosystems and in chemical laboratories, and experimental results from either milieu are often reported as mean values and their associated variances. Probabilistic modeling techniques (e.g. Monte-Carlo simulations) can account, in principle, for this variation and attach an error bound or confidence interval to each important output variable. Monte-Carlo simulation is, however, very time-consuming (i.e., expensive), and the statistical distributions of chemical and environmental parameters are not often known in the requisite detail. The objective of this kind of modeling, in the case of hazard evaluations, would in any case be to estimate the effect of parameter errors on the overall conclusions to be drawn from the model. This goal can be met less expensively and more efficiently by some form of sensitivity analysis.

1.4 Sensitivity Analysis and Error Evaluation

EXAMS does not provide a formal sensitivity analysis among its options: the number of sub-simulations needed to fully account for interactions among chemical and environmental variables is prohibitively large (Behrens 1979). When, for example, the second-order rate constant for alkaline hydrolysis of a compound is described to EXAMS via an Arrhenius function, the rate constant computed for each compartment in the ecosystem depends on at least six parameters. These include the frequency factor and activation energy of the reaction, the partition coefficient of the compound (KOCG), the organic carbon content of the sediment phase, the temperature, and the concentration of hydroxide ion. The overall rate estimate is thus as dependent upon the accuracy of the system definition as it is upon the skill of the laboratory chemist; in this example, the rate could vary six orders of magnitude as a function of differences among ecosystems. In order to fully map the parameter interactions affecting a process, all combinations of parameter changes would have to be simulated. Even this (simplified) example would require 63 simulations ((2**n) - 1, where n is the number (6) of parameters) merely to determine sensitivities of a single component process in a single ecosystem compartment.

Sensitivity analysis remains an attractive technique for answering a crucial question that arises during hazard evaluation. This question can be simply stated: "Are the chemical data accurate enough, and precise enough, to support an analysis of the risk entailed by releases of the chemical into the environment?" Like many simple questions, this question does not have a simple, definitive answer. It can, however, be broken down into a series of explicit, more tractable questions whose answers sum to a reasonably complete evaluation of the significance that should be attached to a reported error bound or confidence interval on any input datum. Using the output tables and command language utilities provided by EXAMS, these questions can be posed, and answered, in the following order.

1. Which geographic areas, and which ecosystems, develop the largest chemical residuals? EXAMS allows a user to load the data for any environment contained in his files, specify a loading, and run a simulation, through a simple series of one-line English commands.

2. Which process is dominant in the most sensitive ecosystem(s)? The dominant process, i.e., the process most responsible for the decomposition of the compound in the system, is the process requiring the greatest accuracy and precision in its chemical parameters. EXAMS produces two output tables that indicate the relative importance of each process. The first is a "kinetic profile" (or frequency scaling), which gives a compartment-by-compartment listing with all processes reduced to equivalent (/hr) terms. The second is a tabulation of the overall steady-state fate of the compound, giving a listing of the percentage of the load consumed by each of the transport and transformation processes at steady state.

Given the dominant process, the input data affecting this process can be varied over the reported error bounds, and a simulation can be executed for each value of the parameters. The effect of parameter errors on the EECs and persistence of the compound can then be documented by compiling the results of these simulations.

This sequence of operations is, in effect, a sensitivity analysis, but the extent of the analysis is controlled and directed by the user. In some cases, for example, one process will always account for most of the decomposition of the compound. When the data base for this dominant process is inadequate, the obvious answer to the original question is that the data do not yet support a risk analysis. Conversely, if the dominant process is well defined, and the error limits do not substantially affect the estimates of exposure and persistence, the data may be judged to be adequate for the exposure analysis portion of a hazard evaluation.

1.5 EXAMS Process Models

In EXAMS, the loadings, transport, and transformations of a compound are combined into differential equations by using the mass conservation law as an accounting principle. This law accounts for all the compound entering and leaving a system as the algebraic sum of (1) external loadings, (2) transport processes exporting the compound out of the system, and (3) transformation processes within the system that degrade the compound to its daughter products. The fundamental equations of the model describe the rate of change in chemical concentrations as a balance between increases due to loadings, and decreases due to the transport and transformation processes removing the chemical from the system.

The set of unit process models used to compute the kinetics of a compound is the central core of EXAMS. These unit models are all "second-order" or "system-independent"models: each process equation includes a direct statement of the interactions between the chemistry of a compound and the environmental forces that shape its behavior in aquatic systems. Most of the process equations are based on standard theoretical constructs or accepted empirical relationships. For example, light intensity in the water column of the system is computed using the Beer-Lambert law, and temperature corrections for rate constants are computed using Arrhenius functions. Detailed explanations of the process models incorporated in EXAMS, and of the mechanics of the computations, are presented in Section 2.

1.5.1 Ionization and Sorption

Ionization of organic acids and bases, and sorption of the compound with sediments and biota, are treated as thermodynamic properties or (local) equilibria that constrain the operation of the kinetic processes. For example, an organic base in the water column may occur in a number of molecular species (as dissolved ions, sorbed with sediments, etc.), but only the uncharged, dissolved species can be volatilized across the air-water interface. EXAMS allows for the simultaneous treatment of up to 15 molecular species of a chemical. These include the parent uncharged molecule, and singly- or doubly-charged cations and anions, each of which can occur in a dissolved, sediment-sorbed, or biosorbed form. The program computes the fraction of the total concentration of compound that is present in each of the 15 molecular structures (the "distribution coefficients," ALPHA). These values enter the kinetic equations as multipliers on the rate constants. In this way, the program accounts for differences in reactivity that depend on the molecular form of the chemical. For example, the lability of a particular molecule to hydrolytic decomposition may depend on whether it is dissolved or is sorbed with the sediment phase of the system. EXAMS makes no intrinsic assumptions about the relative transformation reactivities of the 15 molecular species. These assumptions are under direct user control through the way the user structures the input data describing the chemistry of the compound.

1.5.2 Transformation Processes

EXAMS computes the kinetics of transformations attributable to direct photolysis, hydrolysis, biolysis, and oxidation reactions. The input chemical data for hydrolytic, biolytic, and oxidative reactions can be entered either as single-valued second-order rate constants, or as a pair of values defining the rate constant as a function of environmental temperatures. For example, the input data for alkaline hydrolysis of the compound consists of two computer variables: KBHG, and EBHG. When EBHG is zero, the program interprets KBHG as the second-order rate constant. When EBHG is non-zero, EBHG is interpreted as the activation energy of the reaction, and KBHG is re-interpreted as the pre-exponential (frequency) factor in an Arrhenius equation giving the second-order rate constant as a function of the environmental temperature (TCELG) in each system compartment. (KBHG and EBHG are both actually matrices with 15 elements; each element of the matrix corresponds to one of the 15 possible molecular species of the compound.)

EXAMS includes two algorithms for computing the rate of photolytic transformation of a chemical. These algorithms were structured to accommodate the two more common kinds of laboratory data and chemical parameters available to describe photolysis reactions. The simpler of the algorithms (subroutine PHOTO1) requires only an average first-order rate constant (KDPG) applicable to near-surface waters under cloudless conditions at a specified reference latitude (RFLATG). In order to give the user control of reactivity assumptions, KDPG is coupled to user-supplied (normally unit-valued) reaction quantum yields (QUANTG) for each molecular species of the compound. The more complex algorithm (subroutine PHOTO2) computes photolysis rates directly from the absorption spectra (molar extinction coefficients, ABSG) of the compound and its ions and measured values of the reaction quantum yields.

The total rate of hydrolytic transformations is computed by EXAMS as the sum of three contributing processes. Each of these processes can be entered as simple rate constants or as Arrhenius functions of temperature. The rate of specific-acid catalyzed reactions is computed from the pH (PHG) for each sector of the ecosystem, and specific-base catalysis is computed from the environmental pOH (POHG). The rate data for neutral hydrolysis of the compound are entered as a set of pseudo-first-order rate coefficients for reaction of the 15 molecular species with the water molecule.

EXAMS allows the user to compute biotransformation of the compound in the water column, and in the bottom sediments, of the system as entirely separate functions. Both models are second-order equations that relate the rate of biotransformation to the size of the bacterial population actively degrading the compound. The second-order rate constants (KBACWG for the water column, KBACSG for benthic sediments) can be entered either as single-valued constants or as functions of temperature. When a non-zero value is entered for the Q-10 of a biotransformation (parameters QTBAWG and QTBASG, respectively), KBAC is interpreted as the rate constant at 20 degrees C, and the biolysis rate in each sector of the ecosystem is adjusted for the local temperature (BIOTMG).

Oxidation reactions are computed from the chemical input data and the total environmental concentrations of reactive oxidizing species (alkylperoxy and alkoxyl radicals, etc.) specified by the user. The chemical data can again be entered either as simple second-order rate constants or as Arrhenius functions.

1.5.3 Transport Processes

Internal transport and export of a chemical occur in EXAMS via advective and dispersive movement of dissolved, sediment-sorbed, and biosorbed materials and by volatilization losses at the air-water interface. EXAMS provides a set of vectors (JFRADG, etc.) that specify the location and strength of both advective and dispersive transport pathways. Advection of water through the system is then computed from the water balance, using hydrologic data (rainfall, evaporation rates, streamflows, groundwater seepages, etc.) supplied to EXAMS as part of the definition of each environment. Dispersive interchanges within the system, and across system boundaries, are computed from the characteristic length (CHARLG), cross-sectional area (XSTURG), and dispersion coefficient (DSPG) specified for each active exchange pathway. EXAMS can compute transport of a toxicant via whole-sediment bedloads, suspended sediment wash-loads, exchanges with fixed-volume sediment beds, ground-water infiltration, transport through the thermocline of a lake, losses in effluent streams, etc. Volatilization losses are computed using a two-resistance model. This computation treats the total resistance to transport across the air-water interface as the sum of resistances in the liquid and vapor phases immediately adjacent to the interface.

1.5.4 Chemical Loadings

External loadings of a toxicant can enter the ecosystem via point sources (STRLDG), non-point sources (NPSLDG), dry fallout or aerial drift (DRFLDG), atmospheric wash-out (PCPLDG), and via ground-water seepage (IFLLDG) entering the system. Any type of load can be entered for any system compartment, but the program will not implement a loading that is inconsistent with the system definition. For example, the program will automatically cancel a

PCPLD entered for the hypolimnion or benthic sediments of a lake ecosystem. When this type of corrective action is executed, the change is reported to the user via an error message.

1.6 Ecosystems Analysis and Mathematical Systems Models

The EXAMS program was constructed from a systems analysis perspective. Systems analysis begins by defining a system's goals, inputs, environment, resources, and the nature of the system's components and their interconnections. The system goals describe the outputs produced by the system as a result of operating on its input stream. The system environment comprises those factors affecting system outputs over which the system has little or no control. These factors are often called "forcing functions" or "external driving variables." Examples for an aquatic ecosystem include runoff and sediment erosion from its watershed, insolation, and rainfall. System resources are defined as those factors affecting performance over which the system exercises some control. The resources of an aquatic ecosystem include, for example, the pH throughout the system, light intensity in the water column, and dissolved oxygen concentrations. The levels of these internal driving variables are determined, at least in part, by the state of the system itself. In other words, these factors are not necessarily single-valued functions of the system environment. Each of the components or "state variables" of a system can be described in terms of its local input/output behaviors and its causal connections with other elements of the system. The systems approach lends itself to the formulation of mathematical systems models, which are simply tools for encoding knowledge of transport and transformation processes and deriving the implications of this knowledge in a logical and repeatable way.

A systems model, when built around relevant state variables (measurable properties of system components) and causal process models, provides a method for extrapolating future states of systems from knowledge gained in the past. In order for such a model to be generally useful, however, most of its parameters must possess an intrinsic interest transcending their role in any particular computer program. For this reason, EXAMS was designed to use chemical descriptors (Arrhenius functions, pKa, vapor pressure, etc.) and water quality variables (pH, chlorophyll, biomass, etc.) that have been independently measured for many chemicals and ecosystems.

1.6.1 EXAMS Design Strategy

The conceptual view adopted for EXAMS begins by defining aquatic ecosystems as a series of distinct subsystems, interconnected by physical transport processes that move synthetic chemicals into, through, and out of the system. These subsystems include the epilimnion and hypolimnion of lakes, littoral zones, benthic sediments, etc. The basic architecture of a computer model also depends, however, on its intended uses. EXAMS was designed for use by toxicologists and decision-makers who must evaluate the risk posed by use of a new chemical, based on a forecast from the model. The EXAMS program is itself part of a "hazard evaluation system," and the structure of the program was necessarily strongly influenced by the niche perceived for it in this system.

Many intermediate technical issues arise during the development of a systems model. Usually these issues can be resolved in several ways; the modeling "style" or design strategy used to build the model guides the choices taken among the available alternatives. The strategy used to formulate EXAMS begins from a primary focus on the needs of the intended user and, other things being equal, resolves most technical issues in favor of the more efficient computation. For example: all transport and transformation processes are driven by internal resource factors (pH, temperature, water movements, sediment deposition and scour, etc.) in the system, and each deserves separate treatment in the model as an individual state variable or function of several state variables. The strategy of model development used for EXAMS suggests, however, that the only state variable of any transcendent interest to the user is the concentration of the chemical itself in the system compartments. EXAMS thus treats all environmental state variables as coefficients describing the state of the ecosystem, and only computes the implications of that state, as residual concentrations of chemicals in the system.

Although this approach vastly simplifies the mathematical model, with corresponding gains in efficiency and speed, the system definition is now somewhat improper. System resources (factors affecting performance that are subject to feedback control) have been redefined as part of the system environment. In fact, the "system" represented by the model is no longer an aquatic ecosystem, but merely a chemical pollutant. Possible failure modes of the model are immediately apparent. For example, introduction of a chemical subject to alkaline hydrolysis and toxic to plant life into a productive lake would retard primary productivity. The decrease in primary productivity would lead to a decrease in the pH of the system and, consequently, a decrease in the rate of hydrolysis and an increase in the residual concentration of the toxicant. This sequence of events would repeat itself indefinitely, and constitutes a positive feedback loop that could in reality badly damage an ecosystem. Given the chemical buffering and functional redundancy present in most real ecosystems, this example is inherently improbable, or at least self-limiting. More importantly, given the initial EEC, the environmental toxicologist could anticipate the potential hazard.

There is a more telling advantage, moreover, to the use of environmental descriptors in preference to dynamic environmental state variables. Predictive ecosystem models that include all the factors of potential importance to the kinetics of toxic pollutants are only now being developed, and will require validation before any extensive use. Furthermore, although extremely fine-resolution (temporal and spatial) models are often considered an ultimate ideal, their utility as components of a fate model for synthetic chemicals remains suspect. Ecosystems are driven by meteorological events, and are themselves subject to internal stochastic processes. Detailed weather forecasts are limited to about nine days, because at the end of this period all possible states of the system are equally probable. Detailed ecosystem forecasts are subject to similar constraints (Platt et al. 1977). For these reasons, EXAMS was designed primarily to forecast the prevailing climate of chemical exposures, rather than to give detailed local forecasts of EECs in specific locations.

1.6.2 Temporal and Spatial Resolution

When a synthetic organic chemical is released into an aquatic ecosystem, the entire array of transport and transformation processes begins at once to act on the chemical. The most efficient way to accommodate this parallel action of the processes is to combine them into a mathematical description of their total effect on the rate of change of chemical concentration in the system. Systems that include transport processes lead to partial differential equations, which usually must be solved by numerical integration. The numerical techniques in one way or another break up the system, which is continuously varying in space and time, into a set of discrete elements. Spatial discrete elements are often referred to as "grid points" or "nodes", or, as in EXAMS, as "compartments." Continuous time is often represented by fixing the system driving functions for a short interval, integrating over the interval, and then "updating" the forcing functions before evaluating the next time-step. At any given moment, the behavior of the chemical is a complicated function of both present and past inputs of the compound and states of the system.

EXAMS is oriented toward efficient screening of a multitude of newly invented chemicals. Ideally, a full evaluation of the possible risks posed by manufacture and use of a new chemical would begin from a detailed time-series describing the expected releases of the compound into aquatic systems over the entire projected history of its manufacture. Given an equivalently detailed time-series for environmental variables, machine integration would yield a detailed picture of EECs in the receiving water body over the entire period of concern. The great cost of this approach, however, militates against its use as a screening tool. Fine resolution evaluation of synthetic chemicals can probably be used only for compounds that are singularly deleterious and of exceptional economic significance.

The simplest situation is that in which the chemical loadings to systems are known only as single estimates pertaining over indefinite periods. This situation is the more likely for the vast majority of new chemicals, and was chosen for development of EXAMS. It has an additional advantage. The ultimate fate and exposure of chemicals often encompasses many decades, making detailed time traces of EECs feasible only for short-term evaluations. In EXAMS, the environment is represented via long-term average values of the forcing functions that control chemical's behavior. By combining the chemistry of the compound with average properties of the ecosystem, EXAMS reduces the screening problem to manageable proportions. These simplified "first-order" equations are solved algebraically to give the ultimate (i.e., steady-state) EECs that will eventually result from the input loadings.

Transport of a chemical from a loading point into the bulk of the system takes place by advected flows and by turbulent dispersion. The simultaneous transformations presently result in a continuously varying distribution of the compound over the physical space of the system. This continuous distribution of the compound can be described via partial differential equations. In solving the equations, the physical space of the system must be broken down into discrete elements. EXAMS is a compartmental or "box" model. The physical space of the system is broken down into a series of physically homogeneous elements (compartments) connected by advective and dispersive fluxes. Each compartment is a particular volume element of the system, containing water, sediments, biota, dissolved and sorbed chemicals, etc. Loadings and exports are represented as mass fluxes across the boundaries of the volume elements; reactive properties are treated as point processes within each compartment.

In characterizing aquatic systems for use with EXAMS, particular attention must be given the grid-size of the spatial net used to represent the system. In effect, the compartments must not be so large that internal gradients have a major effect on the estimated transformation rate of the compound. In other words, the compartments are assumed to be "well-mixed," that is, the reaction processes are not slowed by delays in transporting the compound from less reactive to more reactive zones in the volume element. Physical boundaries that can be used to delimit system compartments include the air-water interface, the thermocline, the benthic interface, and perhaps the depth of bioturbation of sediments. Some processes, however, are driven by environmental factors that occur as gradients in the system, or are most active at interfaces. For example, irradiance is distributed exponentially throughout the water column, and volatilization occurs only at the air-water interface. The rate of these transformations may be overestimated in, for example, quiescent lakes in which the rate of supply of chemical to a reactive zone via vertical turbulence controls the overall rate of transformation, unless a relatively fine-scale segmentation is used to describe the system. Because compartment models of strongly advected water masses (rivers) introduce some numerical dispersion into the calulations, a relatively fine-scale segmentation is often advisable for highly resolved evaluations of fluvial systems. In many cases the error induced by highly reactive compounds will be of little moment to the probable fate of the chemical in that system, however. For example, it makes little difference whether the photolytic half-life of a chemical is 4 or 40 minutes; in either case it will not long survive exposure to sunlight.

1.6.3 Model Assumptions

EXAMS, like all models, is based upon a number of assumptions. The program has been designed to evaluate long-term, steady loadings of chemicals that result in trace-level EECs in aquatic systems. EXAMS generates a steady-state, average flow field for the ecosystem. The program cannot evaluate the transient concentrated EECs that arise, for example, from spills of toxic chemicals. This limitation arises from two factors: First, a steady flow field is not always appropriate for evaluating the spread and decay of a major pulse (spill) input. Second, the assumption of trace-level EECs, which can be violated by spills, has been used to design the process equations used in EXAMS. The following assumptions were used to build the model.

(1) A first-order evaluation can be executed independently of the chemical's actual effects on the system. In other words, the chemical does not itself radically change the environmental variables that drive its transformations. Thus, for example, an organic acid or base is assumed not to change the pH of the system, the compound is assumed not to itself absorb a significant fraction of the light entering the system, and bacterial populations do not grow (or decline) simply due to the presence of the chemical.

(2) EXAMS uses linear sorption isotherms, and second-order (rather than Michaelis-Menten-Monod) expressions for biolysis. This approach is known to be valid for low concentrations of pollutants; its validity at high concentrations is less

certain. EXAMS controls its computational range to ensure that this assumption is not grossly violated. The program will not report EECs for loadings that result in aqueous-phase chemical residuals greater than 50% of the aqueous solubility of the compound, or 1.E-5 M in the dissolved neutral (uncharged) form of the compound. This restraint incidentally allows the model to ignore precipitation of the compound from solution, and precludes inputs of solid particles of the chemical.

(3) Sorption is treated as a thermodynamic or constitutive property of each compartment in the system, that is, sorption/desorption kinetics are assumed to be rapid compared to other processes. The adequacy of this assumption is partially controlled by properties of the compound and system being evaluated. Extensively sorbed chemicals tend to be sorbed and desorbed more slowly than weakly sorbed compounds; desorption half-lives may approach 40 days for the most extensively bound chemicals. Experience with the program has indicated, however, that strongly sorbed chemicals tend to be captured by benthic sediments, where their release to the water column is controlled by benthic exchange processes. This phenomenon overwhelms any accentuation of the speed of processes in the water column that may be caused by the assumption of local equilibrium.

SECTION 2

FUNDAMENTAL THEORY

Many excellent books, review articles, and journal reports have been written on the subject of the fate and transport of chemicals in the environment. This report is not intended as an exhaustive summary of the ideas and factual information available from the literature. EXAMS is a distillation of that literature, encoded in a computer program. This Section of the report is a summary of the fundamental ideas that were used to construct the EXAMS program. The references cited represent only the key findings or papers that directly influenced the EXAMS code. Additional detail and background information can be found in the works listed in the bibliography for this report.

2.1 Compartment Models and Conservation of Mass

EXAMS' environmental data are contained in a file (the "canonical environments file") that includes a series of concise descriptions of the aquatic systems of interest to a user. (The term "canonical" simply means that the data in the file includes only those quantities bearing directly on the fate and transport of synthetic organic chemicals.) Each water-body is represented via a set of N compartments or distinct zones in the system. The program is based on a series of mass balances, which give rise to a single differential equation for each compartment. Working from the transport and transformation process equations, EXAMS compiles an equation for the net rate of change of chemical concentration in each compartment. The resulting system of N differential equations describes a mass balance for the entire ecosystem. These equations have the general form of Equation 2.1:

Eq. 2.1 $$V\,(d[C]/dt) = Le + Li - (V)(K)[C]$$

where:

V is the volume of water in the compartment (liters),
[C] is the total chemical concentration as mg/liter of V,
Le is the total external loading on the compartment (mg/hr),
Li is the total internal loading on the compartment (mg/hr) resulting from contaminated flows among system compartments, and

K is an overall pseudo-first-order (/hr) loss constant that expresses the combined effect of transport and transformation processes that decrease chemical concentration.

The "canonical environments file" currently supplied with the EXAMS computer program is intended solely as a series of test values to establish that the program is operating correctly. Although the data supplied in this file are within the range of observed values, this file is not intended for production runs of the program. EXAMS has been designed to accept standard water-quality parameters and system characteristics that are commonly measured by limnologists throughout the world. EXAMS also includes a descriptor language (parameters JFRADG, JTURBG, etc.) that simplifies the specification of system geometry and connectedness. The procedure for defining an EXAMS environment is illustrated in Section 3. The EXAMS code has been written in a general (N-compartment) form; the program can be modified and recompiled to handle up to 999 compartments. The program is available in 10-, 50-, and 100-compartment versions.

The chemical data base supplied with the program includes 11 compounds investigated by Smith and coworkers (1978). As with EXAMS' nominal environmental data base, these data should not be regarded as immutably fixed. In many instances the data of Smith et al. (1978) were augmented in order to illustrate EXAMS' data entry capabilities, and the assumptions used to fill gaps in the chemical data base are open to revision as additional experimental data become available.

2.2 Equilibrium Processes

The kinetic properties of organic chemicals are often strongly influenced by the molecular state of the compound. Consider, for example, a compound that can both ionize, and sorb to suspended sediments. In this case, the compound will be present in the water column in ionized, unionized, and sorbed states. In inland waters, where aerosol formation can be neglected, only the unionized, unsorbed molecule can be volatilized across the air-water interface. An accurate evaluation of the tendency of the compound to volatilize thus cannot be obtained until ionization and sorption are incorporated in the estimation method. Ionization and sorption also affect the reactivity of chemicals to transformation processes, but the magnitude of the changes cannot be as readily predicted.

Laboratory determinations of kinetic rate constants are often limited to homogeneous phase (clean water) investigations. Modeling the behavior of a compound in real systems requires some knowledge, or some assumptions, about the effects of sorption and ionization on a chemical's behavior in the environment. EXAMS does not contain "hard-wired" assumptions that sorption either "protects" the compound, enhances its reactivity, or has no effect. Instead, the input chemical data include separate rate constants for each molecular form of the compound. This data array allows a user to include unique rate constants for ions and sorbed molecules when these are known. When heterogeneous phase (or pH dependent) chemical data are not available, the necessary assumptions are left to the user's discretion.

Ionization and sorption of synthetic chemicals are treated as thermodynamic or constitutive properties of each ecosystem compartment in EXAMS. EXAMS treats these processes as local (within-compartment) equilibria, rather than calculating a global (system-wide) partitioning of the compound among its possible molecular species. The alternative of global partitioning or full system-wide equilibria has also been used in the context of evaluative models (e.g., Mackay 1979). As noted by their authors, this assumption neglects effects of intra-system transport and environmental heterogeneity.

Ionization equilibria are usually achieved within a very short time, compared to the time-scale of transport and transformation processes, so a (local) equilibrium assumption is usually justified in natural systems. Desorption of neutral molecules bound to sediments, however, is relatively slow for compounds that are extensively bound (large partition coefficients). EXAMS' evaluations do not explicitly include the effects of sorption/desorption kinetics on transport or transformation processes. The program does, however, compute some major kinetic effects of slow desorptions, as an implicit function of interactions between benthic sediments and the overlying water column.

Extensively sorbed compounds are usually predominantly captured by the bottom sediments (benthic compartments) in an aquatic system. Release of the compound to the water column is then limited by the turnover rate of the bottom sediments themselves. The turnover times of benthic sediments are usually longer than the desorption half-lives of organic chemicals. Consequently, the major kinetic limitations imposed by residence in bottom sediments generally exceed those attributable to desorption kinetics as such.

EXAMS allows for the existence of four ionized species, in addition to the parent unionized molecule. Each of these can partition onto the sediment phase, and the biota, in an ecosystem compartment. The program computes the fraction of the total chemical concentration present in each molecular structure. These distribution coefficients (ALPHA) are used as multipliers on the user-specified transformation rate coefficients for each decomposition process.

2.2.1 Ionization Reactions

According to the Bronsted-Lowry concept of ionization reactions, acids and bases react with solvent (water) to form a conjugate acid-base pair (Stumm and Morgan 1970). The EXAMS program regards any synthetic organic as potentially capable of acting as an ampholyte, and forming both singly and doubly charged cations and anions in an aqueous medium. The unionized molecule is taken as the parent compound, and is denoted in the program documentation as "SH2." The potential acid-base reactions are then:

(1) Basic reactions:

Eq. 2.2 (a) $(SH_2) + (H_2O) \longleftrightarrow (SH_3^+) + (OH^-)$

Eq. 2.3 (b) $(SH_3^+) + (H_2O) \longleftrightarrow (SH_4^{++}) + (OH^-)$

(2) Acidic reactions:

Eq. 2.4 (a) $(SH_2) + (H_2O) \longleftrightarrow (SH^-) + (H_3O^+)$

Eq. 2.5 (b) $(SH^-) + (H_2O) \longleftrightarrow (S^=) + (H_3O^+)$

This set of chemical reactions describes the simultaneous existence of five chemical species of the compound. These species are: (1) the unionized parent molecule SH_2, (2) a singly charged cation SH_3^+, (3) a doubly charged cation SH_4^{++}, (4) a singly charged anion SH^-, and (5) a doubly charged anion $S^=$.

(Again, because EXAMS is an interactive program in which the user has direct access to the input data base, much of this documentation has been written using the computer variables as identifiers and as quantities in the process equations. Although this approach poses some difficulties for the casual reader, it allows the potential user of the program to see the connenctions between program variables and the underlying process theory. The Glossary section of this document contains an alphabetical listing and definitions of EXAMS' input variables. In most cases, direct input data are named with a terminal "G" ("Global"), and variables internal to the EXAMS program itself are named with a terminal "L" ("Local"). For example, "KPSG" can be specified by the user; "KPSL" is its internal equivalent.)

Most compounds do not exhibit the full range of behaviors given in Equations 2.2--2.5. EXAMS' chemical input data stream carries, for each chemical, a vector (SPFLG) of 5 flags that tells the program which of the ionization reactions are appropriate for that compound. (A "flag" in this usage means a signal used to control execution of the program.) Setting an element of the SPFLG vector to "1" indicates that the corresponding chemical species in fact exists; setting an element of SPFLG to "0" (zero) indicates the chemical species does not exist. SPFLG(1) should usually be set to indicate the existence of the parent molecule. When, for example, the remaining flags (SPFLG(2), (3), (4), and (5)) are all zero, EXAMS treats the chemical as a neutral (unionizable) organic compound. Again, when SPFLG(2) is set (=1), and SPFLG(3), (4), and (5) are 0, the compound is taken to be an organic base forming only a singly charged cation (SH_3^+).

The equilibrium constants for the ionization reactions provide a measure of the strength of the organic acid/base relative to water. The basicity constants corresponding to Equations 2.2 and 2.3 are:

Eq. 2.2.1 $K_{b1} = [SH_3^+]\{OH^-\} / [SH_2]\{H_2O\}$

Eq. 2.3.1 $K_{b2} = [SH_4^{++}]\{OH^-\} / [SH_3^+]\{H_2O\}$

The acidity constants corresponding to Equations 2.4 and 2.5 are:

Eq. 2.4.1 $K_{a1} = [SH^-]\{H^+\} / [SH_2]\{H_2O\}$

Eq. 2.5.1 $K_{a2} = [S^=]\{H^+\} / [SH^-]\{H_2O\}$

These ionization constants are "mixed" constants (Stumm and Morgan 1970:82), which take $pH = -\log\{H^+\}$ ($\{H^+\}$ is hydrogen ion activity, IUPAC convention), and the compound is expressed in concentration units. (Salt effects on pK values, and changes in pKw with temperature, are currently neglected in EXAMS.)

In dilute aqueous solutions (unit water activity, $\{H_2O\}=1$), the water terms in the equilibrium constants can be neglected. In benthic sediments, however, much of the compartment volume is occupied by solids, and the decreased activity of water must be considered. In EXAMS, this problem is overcome by referring all concentrations to the aqueous phase of the compartment (note dimensions of variables in Equation 2.1).

Basicity and acidity constants are entered to EXAMS as the negative of their Briggsian logarithms, that is, as pK values. The computer variables are PKBG(1) and PKBG(2) for the first and second basicity constants (generating SH_3^+ and SH_4^+, respectively) and PKAG(1) and PKAG(2) for the first and second acidity constants (generating SH^- and $S^=$, respectively). The equilibrium constants can be entered either as single (temperature-independent) pK values or as functions of temperature. Temperature dependencies of the equilibrium constants are computed from an integrated form of the Gibbs-Helmholtz equation (Castellan 1964:215-217). Each computer input datum (PKBG, PKAG) has a corresponding enthalpy variable

(EPKBG, EPKAG). When the enthalpy term (EPK) is zero, the PK datum is taken as a temperature-independent pK. When the EPK term is non-zero, the PK datum is interpreted as the constant in the equation describing the equilibrium constant as a function of temperature. For example: The Handbook of Chemistry and Physics, Ed. 51 p. D122 (Weast 1971), gives the following data for the second acidity constant of phenol-sulfonic acid.

T(deg. C):	0	5	10	15	20	25	30	35	40	45	50
K(X1.E10):	4.45	5.20	6.03	6.92	7.85	8.85	9.89	10.9	12.0	13.1	14.2

EXAMS could be loaded with a typical value drawn from this data set, for example, at 25 degrees K = 8.85E-10 and PKAG(2) = 9.05 (also load EPKAG(2) = 0.0). The pKa will then be taken as 9.05 regardless of the water temperature of the compartment.

Alternatively, the visible dependence of the acidity constant on temperature could be described to EXAMS via PKAG(2) and a non-zero value of EPKAG(2). Statistical regression of this data on the model

$$Ka = A \exp(-B/RT)$$

where R is the gas constant (1.9872 cal/deg mol) and T is absolute temperature, yields the parameters

$$A = 8.2724E-07$$

and

$$(B/R) = 2.0466E+03$$

and accounts for 99.7% of the variation in Ka. EXAMS requires the logarithm of A, and B in kcal/mol, as input data. Therefore, the dependence of Ka on temperature would be described to EXAMS via

$$PKAG(2) = \log A = -6.082$$

and

$$EPKAG(2) = (B/R) * R * 0.001(cal/kcal) = 4.067 \text{ kcal/mol}$$

EXAMS will then compute a local value of Ka as a function of the water temperature (TCELG) in each system compartment, using the equation:

Eq. 2.6 log(Ka)=PKAG(2)-[1000.*EPKAG(2)/(2.303*R*(TCELG+273.15))]

2.2.2 Sediment Sorption

EXAMS computes a (local) equilibrium value for the partitioning of each chemical species (SH2, SH3+, etc.) to sediment phases in the system. The chemical input data includes a vector of partition coefficients (KPSG) whose elements apply to each of the corresponding chemical species. That is, KPSG(1) is the partition coefficient for neutral organics or the unionized molecule (SH2), KPSG(2) applies to the SH3+ molecule, etc.

EXAMS uses linear isotherms for all sorption computations, rather than the non-linear Freundlich or Langmuir formulations. (A linear isotherm is equivalent to a partition coefficient.) Linear isotherms are usually an adequate descriptor of the capture of neutral organics by sediments, at least up to 50% of their water solubility or 1.E-5 M (Karickhoff 1980 (oral comm.)). EXAMS restricts its operating range to ensure that this assumption is not violated. These restrictions are imposed by evaluating the external loadings to ensure that the inputs to the system are not excessive, and by a pre-output evaluation of the computed EECs in all compartments. Excessive loadings are reduced to one-half their maximum permissible value in the inlet carrier flow (see Section 2.4).

The uptake of neutral organic chemicals by soils and aquatic sediments apparently involves dissolution of the compound into the organic matrix of the soil/sediment, rather than a pure physical (surface) adsorption (see, for example, Chiou, Peters, and Freed 1979). Sorption of this class of chemical probably takes place by a hydrophobic mechanism, in which the compound (or more generally the SH2 molecule of acids and bases) is driven from the water phase of the system by a large fugacity. This process is conceptually similar to the extraction and recovery of an organic pollutant from water using an organic solvent.

The partition coefficent (KPSG) for a particular compound can be normalized to the organic content of soils (Chiou, Peters, and Freed 1979) or, equivalently, to the organic carbon content of aquatic sediments (Karickhoff, Brown, and Scott 1979). The resulting parameter (KOCG) is a relatively stable, system-independent measure of an instrinsic property of organic compounds. KOCG can be used to compute a partition coefficient (KPSL) for sediment phases of an aquatic system, as a function of the organic carbon content (FROCG, organic carbon as fraction of dry weight) of the sediment phase of each compartment.

KOCG is strongy correlated with the octanol-water partition coefficient (KOWG) (Karickhoff, Brown, and Scott 1979). For whole sediments, as used in EXAMS, KOCG can be reliably estimated as 41% of KOWG (Karickhoff, in prep.).

EXAMS computes the SH2 partition coefficent (KPSL(1)) for each system compartment via an hierarchical evaluation of these input data (KPSG(1), KOCG, KOWG). KOCG is the preferred datum, and if it is non-zero, a local (compartment-specific) KPSL(1) is computed from KOCG and the organic carbon content (FROCG) of the sediment phase of each compartment. When KOCG is zero, but the

KOWG entry is non-zero, KPSL(1) is computed as 0.41*KOWG*FROCG. The KPSG datum is used as a system-wide partition coefficient only when both KOCG and KOWG are zero entries. Thus when an observed KPSG is preferred for some user application, both KOCG and KOWG should be omitted from the input data (that is, set to zero) because, otherwise, the preferred computations will override the user's intentions.

Organic ions can exchange with the normal soil ions, to an extent probably governed by the ion exchange capacity of a sediment. The particle-size distribution of the sediment, however, apparently also governs the ability of the sediment to take up organic ions (Karickhoff and Brown 1978). The complexity of this process has hindered the development of robust, system-independent analogs of KOCG for organic ions.

EXAMS includes a series of (admittedly somewhat speculative) "system-independent" measures of ion sorption that can be invoked at the user's option. These parameters relate the KPSL for the organic ions to the ion exchange capacities of sediment phases in each system compartment. The computer variables are:

KCEC(1) for sorption of SH3+; KPSL(2) computed from CECG
KCEC(2) for sorption of SH4++; KPSL(3) computed from CECG
KAEC(1) for sorption of SH-; KPSL(4) computed from AECG
KAEC(2) for sorption of S=; KPSL(5) computed from AECG

The units of KCEC and KAEC are ((mg/kg)/(mg/L)/(meq/100 g dry weight); the cation (CECG) and anion (AECG) exchange capacities of system sediments are entered as milliequivalents (meq) per 100 grams dry weight of the sediment. When a measured partition coefficient is preferred for all sediments in the system, it should be loaded via the appropriate element of the KPSG vector and the corresponding element in KCEC or KAEC should be set to zero.

EXAMS uses the partition coefficient (KPS) for each chemical species, however computed, to calculate the equilibrium sediment sorption of each species on each particulate sediment phase (P) in the system. The chemical equations and equilibrium expressions are similar for each chemical species:

Eq. 2.7 (SH2) + (P)<--->(SH2P) KPS(1) = [SH2P]/[SH2][P]

Eq. 2.8 (SH3+) + (P)<--->(SH3P+) KPS(2) = [SH3P+]/[SH3+][P]

Eq. 2.9 (SH4++) + (P)<--->(SH4P++) KPS(3) = [SH4P++]/[SH4++][P]

Eq. 2.10 (SH-) + (P)<--->(SHP-) KPS(4) = [SHP-]/[SH-][P]

Eq. 2.11 (S=) + (P)<--->(SP=) KPS(5) = [SP=]/[S=][P]

Sediment partition coefficients are usually reported as a ratio of the concentration of sorbed chemical (mg compound/g dry weight of sediment) to the residual aqueous phase concentration (mg/liter), in "dimensionless" units ((mg/kg)/(mg/L)). The sorption equilibrium constants are equivalent to conventional partition coefficients only so long as the concentration of particulate matter [P] is expressed as a "sediment-water ratio" (kg dry weight/ liter of water), and the chemical concentrations (e.g., [SH2P] and [SH2]) are referred to the aqueous phase of the system and expressed as (mg compound/liter of water). EXAMS adheres to this convention for its internal computations. EXAMS' output tables, however, are converted to conventional reporting units. For example, concentrations of sediment-sorbed chemicals are reported to the user as mg/kg dry weight of sediment, but are carried internally as (sorbed mg)/(liter of water).

The need for strict adherence to this convention arises from the very large sediment/water ratios of benthic sediments. Water column compartments can be assumed to have a water volume essentially the same as their environmental volume (VOLG). For these compartments, EXAMS' internal variable (SEDCOL, the sediment/water ratio (kg/L)) is simply computed as 1.E-6 times the input datum (SDCHRG, suspended sediments in mg/L).

Because the solid phase occupies a significant fraction of the total environmental volume of bed sediments, SEDCOL is computed quite differently for benthic (TYPEE "B") compartments. For benthic compartments, the input datum SDCHRG is the bulk density of the sediment (g/cc environmental volume). The sediment/water ratio is computed from the bulk density and water content (PCTWAG, 100 * the fresh weight/dry weight ratio) of the sediment, and the total environmental volume (VOLG, cubic meters) of the compartment. (The computation takes the density of water as 1 g/cc.) The equations are:

Eq. 2.12 SEDCOL = SEDMSL/WATVOL, where

Eq. 2.12.1 TOTMAS = SDCHRG*VOLG*1000.

Eq. 2.12.2 SEDMSL = TOTMAS/(PCTWAG/100.), and

Eq. 2.12.3 WATVOL = TOTMAS - SEDMSL

In these equations, TOTMAS is the total compartment mass (kg), SEDMSL is the mass of sediment in the compartment (kg), and WATVOL is the volume of water contained in the compartment (liters).

The sediment/water ratio can also be computed directly from the water content of the sediment (Equation 2.13).

Eq. 2.13 SEDCOL = 1/((PCTWAG/100) - 1)

Equation 2.12 is the more efficient computation for EXAMS, however, because the results of the intermediate computations (WATVOL, SEDMSL) are used elsewhere in the program.

2.2.3 Biosorption

The uptake of chemicals by living organisms is represented in EXAMS via five simple bioconcentration factors or biomass partition coefficients (KPBG). KPBG is a vector of 5 elements, each of which applies to the corresponding chemical species (SH2, SH3+, etc.). The chemical equations and equilibrium expressions are analogous to those for sediment sorption:

Eq. 2.14 (SH2) + (B)<--->(SH2B) KPB(1) = [SH2B]/[SH2][B]

Eq. 2.15 (SH3+) + (B)<--->(SH3B+) KPB(2) = [SH3B+]/[SH3+][B]

Eq. 2.16 (SH4++) + (B)<--->(SH4B++) KPB(3) = [SH4B++]/[SH4++][B]

Eq. 2.17 (SH-) + (B)<--->(SHB-) KPB(4) = [SHB-]/[SH-][B]

Eq. 2.18 (S=) + (B)<--->(SB=) KPB(5) = [SB=]/[S=][B]

Bioaccumulation factors (KPBG) should be entered to EXAMS on a dry weight basis. The expected units of KPBG are (ug/g(dry))/(mg/L), or the numerically equivalent unit (mg/kg(dry))/(mg/L). As with sediment sorption, EXAMS converts its input data for compartment biomasses (BIOMSG) to an internal variable (BIOTOL, "B" in Eqs. 2.14--2.18) with dimensions of kg dry weight per liter of water in the compartment. EXAMS' input datum for water column compartments (BIOMSG in mg dry weight per liter) is simply multiplied by 1.E-6 (kg/mg) to yield BIOTOL in its proper units. For benthic compartments, the benthic biomass (BIOMSG) is entered to EXAMS with dimensions of grams (dry weight) per square meter of bottom sediment surface. EXAMS converts this datum to its internal units (BIOTOL, kg per liter of interstitial water) via Equation 2.19:

Eq. 2.19 BIOTOL = (AREAG * BIOMSG * 0.001 (kg/g)) / WATVOL

where AREAG is the (user-supplied) total surface area of the benthic compartment (square meters).

The actual quantities of synthetic organics captured by the biomass are often relatively small, compared to the amounts sorbed with sediments or dissolved in the aqueous phase of real systems. Thus, the biomass often plays a relatively insignificant role as a transport or capture medium affecting the fate of an organic pollutant. The role of the biomass as a food-chain vector can, however, have great ecotoxicological significance. (Biotransformation of chemicals is, of course, another matter altogether (see Section 2.3.6).) EXAMS nevertheless accounts, to some extent, for the physical transport of biosorbed chemical. The biomass in each ecosystem compartment is segregated into a resident (fixed in place), and a transportable (planktonic) fraction, via the input parameter PLRAG. EXAMS does not include a mobile component of the biomass, that is, volitional movements of fishes (etc.) among compartments are not assessed. (The transport equations are discussed in Section 2.3.1.)

The opportunity to enter a KPBG vector for organic compounds is provided primarily as a convenience for the user who wishes to estimate organismic body-burdens from simple bioconcentration factors. Note, however, that EXAMS' computations are based simply on partitioning ratios to dissolved species of the chemical. EXAMS does not attempt to evaluate such things as the exposure of fishes to variable chemical concentrations as they migrate among different zones of the ecosystem, or food-chain biomagnifications.

2.2.4 Equilibrium Distribution Coefficients

This Section (2.2.4) is a full derivation of the multi-phase equilibrium equations used in the EXAMS simulation code. It is included here only in the interest of a complete documentation of the program. Discussion of EXAMS' underlying theory resumes in Section 2.3.

EXAMS computes the distribution of the chemical among its 15 possible molecular structures (SH2, SH2P, etc.). This distribution is expressed as a vector of concentration ratios (ALPHA). Each element of ALPHA is the ratio of the concentration of a particular molecular species, to the total concentration of chemical in the system compartment (St, mg chemical per liter of water in the compartment). These ALPHA values enter the kinetic equations as multipliers on the user-supplied rate constants for transformation of each molecular species.

The logic of these computations can best be seen via a sample calculation. For example, consider the behavior of an organic acid in pure water, subject to the following ionization reactions:

Eq. 2.20 $(SH2) + (H2O) \longleftrightarrow (SH-) + (H3O+)$

Eq. 2.21 $(SH-) + (H2O) \longleftrightarrow (S=) + (H3O+)$

In order to evaluate the effects of ionization on transformation and transport of the chemical, EXAMS requires three concentration ratios (R):

Eq. 2.22 (1) the fraction present as SH2, or R(1) = [SH2]/[St]

Eq. 2.23 (2) the fraction present as SH-, or R(2) = [SH-]/[St]

Eq. 2.24 (3) the fraction present as S=, or R(3) = [S=]/[St]

The equilibrium constants for the chemical equations 2.20 and 2.21 are:

Eq. 2.25 Ka1 = [SH-]{H+}/[SH2]

Eq. 2.26 Ka2 = [S=]{H+}/[SH-]

As has already been mentioned, EXAMS computes {H+} as 10.**(-PHG). The equilibrium expressions, together with a concentration condition, provide enough information for computing the desired concentration ratios R (Stumm and Morgan 1970:102). The concentration condition is simply a statement of the law of conservation of mass:

Eq. 2.27 [St] = [SH2] + [SH-] + [S=]

The concentration condition (Eq. 2.27) and the definition of the first concentration ratio R(1) (Eq. 2.22) combine to give:

Eq. 2.28 R(1) = [SH2] / ([SH2] + [SH-] + [S=])

The equilibrium expressions can now be solved for [SH-] and [S=] in terms of [SH2]. To wit, Eq. 2.25 can be rearranged to give:

Eq. 2.29 [SH-] = Ka1[SH2]/{H+}

and, from Eq. 2.26,

Eq. 2.30 [S=] = Ka2[SH-]/{H+}

Substituting Eq. 2.29 into Eq. 2.30 yields:

Eq. 2.31 [S=] = (Ka1)(Ka2)[SH2]/{H+}{H+}

Substituting Eq. 2.29 and Eq. 2.31 into Eq. 2.28, and cancelling [SH2] from numerator and denominator, yields the desired result:

Eq. 2.32 R(1) = 1/(1 + Ka1/{H+} + (Ka1)(Ka2)/{H+}{H+})

The second distribution coefficient R(2) can be computed in an analogous fashion. From the definition of R(2) in Eq 2.23, and the concentration condition (Eq. 2.27),

Eq. 2.33 R(2) = [SH-]/[St] = [SH-] / ([SH2] + [SH-] + [S=])

Solving Eq. 2.25 for [SH2], and Eq. 2.26 for [S=], yields the required expressions in [SH-]:

Eq. 2.34 $$[SH2] = [SH-](H+)/Ka1$$

Eq. 2.35 $$[S=] = Ka2[SH-]/(H+)$$

Substituting Eqs. 2.34 and 2.35 into Eq. 2.33, and cancelling [SH-] from numerator and denominator, then gives an expression for R(2):

Eq. 2.36 $$R(2) = 1 / (\ (H+)/Ka1 + 1 + Ka2/(H+)\ )$$

This conventional solution for the distribution coefficient is somewhat unsatisfying for execution in a computer program, however. Whenever the acidity constant (Ka1) is zero, the machine will, nonetheless, attempt the division and make an error. Of course, a separate segment of code could be written for each possible subset of the 15 potential molecular species, and the machine could be guided to the appropriate section of the code by a series of conditional branches or a logic tree. Observe, however, that Eq. 2.36 can also be written as:

Eq. 2.37 $$R(2) = (Ka1/(H+))\ /\ (1 + Ka1/(H+) + (Ka1)(Ka2)/(H+)(H+))$$

This equivalent expression can be generated by simply substituting the second term in the denominator of Eq. 2.32 into its own numerator. Eq. 2.37 now has the advantage that a zero value for Ka1 will not cause the computer to attempt a "zero divide," and will nonetheless yield the proper value for R(2), that is, zero.

In the same way, substitution of the third term in the denominator into the numerator of Eq. 2.32 gives:

Eq. 2.38 $$R(3) = \frac{(Ka1)(Ka2)/(H+)(H+)}{1 + Ka1/(H+) + (Ka1)(Ka2)/(H+)(H+)}$$

Eq. 2.38 is equivalent to the expression for R(3) obtained via substitution of expressions for [SH2] and [SH-] (in terms of [S=]) into the formula for R(3) given by:

Eq. 2.39 $$R(3) = [S=]/[St] = [S=]\ /\ (\ [SH2] + [SH-] + [S=]\ )$$

Rearranging Eq. 2.26 gives [SH-] in terms of [S=]:

Eq. 2.40 $$[SH-] = [S=](H+)/Ka2$$

and Eq. 2.25 gives:

Eq. 2.41 $$[SH2] = [SH-](H+)/Ka1$$

or, substituting Eq. 2.40 into Eq. 2.41,

Eq. 2.42 [SH2] = [S=](H+)(H+) / (Ka1)(Ka2)

Substituting Eqs. 2.40 and 2.42 into Eq. 2.39, and cancelling [S=] from numerator and denominator, then yields:

Eq. 2.43 R(3) = 1 / ((H+)(H+)/(Ka1)(Ka2) + (H+)/Ka2 + 1)

which is equivalent to Eq. 2.38.

This example demonstrates that an algorithm for computing the distribution coefficients (ALPHA) of any multi-species mixture can be constructed in the following way.

(1) Write a concentration condition for [St] that expresses the law of conservation of mass (Eq. 2.27).

(2) Define the distribution coefficient for the parent molecule (SH2) as [SH2]/[St] (Eq. 2.28).

(3) Solve the equilibrium expressions for the full system (Eq. 2.25 and Eq. 2.26) for each molecular species, expressing each species in terms of [SH2] (Eq. 2.29 and Eq. 2.31).

(4) Cancel [SH2] from each of these expressions (Eq. 2.29 and 2.31), thereby obtaining the contribution of each species (DISFCT(I)) to the denominator of Eq. 2.32.

(5) Compute a total denominator (SUMFCT) as (1 + these terms), as in Eq. 2.32 (that is, DISFCT(1) = [SH2]/[SH2] = 1).

(6) Compute each distribution coefficient (ALPHA(I)) as DISFCT(I)/SUMFCT, where DISFCT(1) = 1 and, in this example, DISFCT(2) = Ka1/(H+) and DISFCT(3) = (Ka1)(Ka2)/(H+)(H+)

This computational procedure is general for all its subsets: when any Ka = 0, the computed distribution coefficient is zero. Furthermore, the ALPHA values always sum to 1.0, as they must in order to conform to the law of conservation of mass.

The EXAMS algorithm for computing distribution coefficients of the 15 (potential) molecular species of an organic chemical was constructed on this model. The full concentration condition is:

Eq. 2.44 [St] = [SH2] + [SH2P] + [SH2B] + [SH3+] + [SH3P+] +
[SH3B+] + [SH4++] + [SH4P++] + [SH4B++] + [SH-] +
[SHP-] + [SHB-] + [S=] + [SP=] + [SB=]

The successive contributions of each molecular species to the denominator of [SH2]/[St] are:

(1) Contribution of [SH2]:

Eq. 2.45 DISFCT(1) = [SH2]/[SH2] = 1.0

(2) Contribution of sediment-sorbed SH2, that is, [SH2P]: from Eq. 2.7,

Eq. 2.46 [SH2P]=[SH2][P](KPS(1)), and DISFCT(2)=(KPS(1))[P]

(Recall that [P] is the sediment/water ratio, SEDCOL.)

(3) Contribution of biosorbed SH2, that is, [SH2B]: from Eq. 2.14,

Eq. 2.47 [SH2B]=[SH2][B](KPB(1)), and DISFCT(3)=(KPB(1))[B]

(Recall that [B] is the biomass/water ratio, BIOTOL.)

(4) Contribution of singly charged cation, [SH3+]: EXAMS computes {OH-}as 10.**(-POHG), and, from Eq. 2.2.1,

Eq. 2.48 [SH3+]= (Kb1)[SH2]/{OH-}, and DISFCT(4)= Kb1/{OH-}

(Recall that all computations are referenced to the aqueous phase of a given compartment, so {H2O} can be taken as 1.)

(5) Contribution of sediment-sorbed singly charged cation, [SH3P+]: from Eq. 2.8,

Eq. 2.49 [SH3P+] = (KPS(2))[SH3+][P]

Substituting Eq. 2.48 into Eq. 2.49 yields

Eq. 2.50 [SH3+P] = (KPS(2))(Kb1)[P][SH2]/{OH-}, and

DISFCT(5) = (KPS(2))(Kb1)[P]/{OH-}

(6) Contribution of biosorbed singly charged cation, [SH3B+]: from Eq. 2.15,

Eq. 2.51 [SH3B+] = (KPB(2))[SH3+][B]

Substitution of Eq. 2.48 into Eq. 2.51 yields:

Eq. 2.52 [SH3B+] = (KPB(2))(Kb1)[B][SH2]/{OH-}, and

DISFCT(6) = (KPB(2))(Kb1)[B]/{OH-}

(7) Contribution of doubly charged cation, [SH4++]: rearranging Eq. 2.3.1 yields:

Eq. 2.53 [SH4++] = Kb2[SH3+]/{OH-}

Substituting Eq. 2.48 into Eq. 2.53 yields:

Eq. 2.54 [SH4++] = (Kb1)(Kb2)[SH2]/{OH-}{OH-}, and

DISFCT(7) = (Kb1)(Kb2)/{OH-}{OH-}

(8) Contribution of sediment-sorbed doubly charged cation, [SH4P++]: rearranging Eq. 2.9 gives:

Eq. 2.55 [SH4P++] = (KPS(3))[P][SH4++]

Substituting Eq. 2.54 into Eq. 2.55 yields:

Eq. 2.56 [SH4P++] = (KPS(3))(Kb1)(Kb2)[SH2][P]/{OH-}{OH-}

and DISFCT(8) = (KPS(3))(Kb1)(Kb2)[P]/{OH-}{OH-}

(9) Contribution of biosorbed doubly charged cation, [SH4B++]: rearranging Eq. 2.16 yields:

Eq. 2.57 [SH4B++] = (KPB(3))[SH4++][B]

Substituting Eq. 2.54 into Eq. 2.57 yields:

Eq. 2.58 [SH4B++] = (KPB(3))(Kb1)(Kb2)[SH2][B]/{OH-}{OH-}

and DISFCT(9) = (Kb1)(Kb2)(KPB(3))[B]/{OH-}{OH-}

(10) Contribution of singly charged anion, [SH-]: Eq. 2.4.1 yields:

Eq. 2.59 [SH-] = (Ka1)[SH2]/{H+}, and DISFCT(10) = Ka1/{H+}

(11) Contribution of sediment-sorbed singly charged anion, [SHP-]: rearranging Eq. 2.10 gives:

Eq. 2.60 [SHP-] = (KPS(4))[SH-][P]

Substituting Eq. 2.59 into Eq. 2.60 yields:

Eq. 2.61 [SHP-] = (KPS(4))(Ka1)[SH2][P]/{H+}, and

DISFCT(11) = (Ka1)(KPS(4))[P]/{H+}

(12) Contribution of biosorbed singly charged anion, [SHB-]: rearranging Eq. 2.17 gives:

Eq. 2.62 [SHB-] = (KPB(4))[SH-][B]

Substitution of Eq. 2.59 into Eq. 2.62 yields:

Eq. 2.63 [SHB-] = (KPB(4))(Ka1)[SH2][B]/{H+}, and

DISFCT(12) = (Ka1)(KPB(4)[B]/{H+}

(13) Contribution of doubly charged anion, [S=]: Eq. 2.5.1 yields:

Eq. 2.64 [S=] = (Ka2)[SH-]/{H+}

Substituting Eq. 2.59 into Eq. 2.64 gives:

Eq. 2.65 [S=] = (Ka1)(Ka2)[SH2]/{H+}{H+}, and

DISFCT(13) = (Ka1)(Ka2)/{H+}{H+}

(14) Contribution of sediment-sorbed doubly charged anion, [SP=]: rearranging Eq. 2.11 gives:

Eq. 2.66 [SP=] = (KPS(5))[S=][P]

Substituting Eq. 2.65 into Eq. 2.66 yields:

Eq. 2.67 [SP=] = (Ka1)(Ka2)(KPS(5))[SH2][P]/{H+}{H+}, and

DISFCT(14) = (Ka1)(Ka2)(KPS(5))[P]/{H+}{H+}

(15) Contribution of biosorbed doubly charged anion, [SB=]: rearranging Eq. 2.18 gives:

Eq. 2.68 [SB=] = (KPB(5))[S=][B]

Substitution of Eq. 2.65 into Eq. 2.68 yields:

Eq. 2.69 [SB=] = (KPB(5))(Ka1)(Ka2)[SH2][B]/{H+}{H+}, and

DISFCT(15) = (Ka1)(Ka2)(KPB(5))[B]/{H+}{H+}

Finally, the total denominator is:

SUMFCT = DISFCT(1) + DISFCT(2) + . . . + DISFCT(15)

and the distribution coefficient, that is, the fraction of the total concentration of compound [St] present in each molecular form, can be simply computed as:

ALPHA(I) = DISFCT(I)/SUMFCT

The subroutine containing this section of the EXAMS code (DISTRB) also computes the fraction of [St] present in all dissolved, sediment-sorbed, and biosorbed species combined. ALPHA(16), for example, is the total dissolved fraction; it is the sum of ALPHA(1), (4), (7), (10), and (13). These summary coefficients are used with the transport equations. ALPHA(16) is coupled to the water motions to compute the transport of dissolved materials, ALPHA(17) is coupled to sediment transport to compute the transport of sediment-sorbed compound, and ALPHA(18) is coupled to the transport of plankton to compute the transport of biosorbed compound.

2.3 Kinetic Processes

"Kinetic" processes, unlike rapid (local) equilibrium processes such as ionization and sorption, occur on time scales that make their time-dependent behavior of direct concern in a hazard evaluation. (Very slow processes, at the further extreme of the temporal spectrum, are usually treated by modelers as absolute constants. For example, changes in the emission of light by the sun (the solar "constant") are usually modeled only by astrophysicists.) The kinetics of the transport regime in aquatic systems, and the kinetics of the transformation processes that degrade a chemical to innocuous forms, are the primary constituents of EXAMS' evaluative capabilities.

2.3.1 Transport

EXAMS includes a simple calculation of steady-state average transport of water, sediments, and planktonic organisms throughout the system. The flows of water, sediments, and plankton act as simple carriers for the dissolved (ALPHA(16)), sediment-sorbed (ALPHA(17)), and biosorbed (ALPHA(18)) forms of the synthetic organic chemical. These carrier flows are ultimately reduced to coefficients that express the effects of transport processes on the kinetics of the chemical; the vector of concentrations of the synthetic organic chemical itself is the only true time-dependent state variable in EXAMS.

A hydrologic sub-program was created for EXAMS in order to minimize the labor necessary to specify, or modify, the physical transport section of EXAMS' environmental data base. This data base is composed primarily of readily available and easily comprehended parameters, such as the volume, mean depth, and surface area of the system compartments. Any of these parameters can be modified by the user as desired. EXAMS then recomputes the exchanges of materials among compartments, and the net transport of materials through the system, in effect creating a new physical model according to the user's modifications.

The hydrologic subroutine operates on three sub-sets of EXAMS' environmental data base. The first sub-set is a description of the volumes of water entering each zone of the system from external sources. The second data sub-set categorizes the geometry of the system, and the properties and distribution of biomass and sediments. The third sub-set contains structural properties of the ecosystem itself. This last (variables JFRADG, JTURBG, etc.) specifies the direction and strength of the flow pathways interconnecting the system compartments. The flow of water through the system compartments is computed from a mass balance on water entering and leaving each segment.

EXAMS' flow pathways can be specified via advective or dispersive equations, or both. (Advection is like a freight train, dispersion is like a drunken walk.) The program uses conventional equations for both processes. Since the volume of the compartments is constant, the law of conservation of mass demands that the hydrologic inputs to a compartment be balanced by advected flows leaving the compartment. The expresssion used for dispersive or turbulent exchanges across compartment boundaries is, as usual:

$$\frac{(\mathrm{DSPG})(\mathrm{XSTURG})}{(\mathrm{CHARLG})}$$

where XSTURG is the cross-sectional area of the exchange boundary (in square meters), CHARLG is the "characteristic length" (meters) along the flow path (that is, the average length of the compartments or the distance between compartment centers, measured along the exchange axis), and DSPG is the eddy dispersion coefficient (square meters/hour). For example, in a simple model of a stratified lake, when XSTURG is the area of the thermocline and CHARLG is one-half the mean depth of the lake, this expression describes the rate of exchange of water between the epilimnion and hypolimnion.

EXAMS also computes sediment transport via the general advective and dispersive equations, but an additional set of transport rules is superimposed on the sediment equations. For example, an advective pathway between water column compartments is permitted to carry along suspended sediments (and plankton) from one compartment to the next. An advective pathway from the water column into a benthic sediment is not allowed to carry sediment with it, however: This kind of pathway is reserved for water seepage into the sediment, and ground-water recharge leaving the system. The sediment transport rules give EXAMS the ability to include riverine sediment wash-loads and bed-loads, groundwater seepage and recharge, and complex exchanges between the water column and benthic sediment deposits driven by physical and biological processes dominant in non-fluvial systems.

EXAMS does not explicitly represent sequential deposition and scour of benthic sediment zones, nor does it allow for a secular accumulation of bottom sediments with consequent burial of sorbed chemicals. In one sense, this limits EXAMS' utility. For example, run-of-the-river flood control reservoirs are very common in the USA, and many of them rapidly accumulate sediments and bury chemicals in their depths. The bottoms of many, if not most, free-flowing rivers and larger lakes accumulate sediments quite slowly, however. In addition, the synthetic chemicals captured by benthic sediments probably are frequently re-exposed to the overlying water column via water turbulence, physical disturbance by demersal fishes, and the internal stirring of sediments by benthic organisms (bioturbation). EXAMS therefore treats benthic sediments as bottom zone compartments with a fixed volume, subject to continual (albeit slow) exchanges with the overlying water column. At least for evaluation and screening purposes, it seemed unwise to suppose that buried synthetic chemicals will never reappear.

Where appropriate, however, net sedimentation and burial of synthetic chemicals can be readily evaluated, for the burial process can be represented via a first-order disappearance of the compound from benthic sediments. For example, given an active sediment depth of 10 cm, and a net burial of 1 mm/yr, the loss coefficient for a synthetic compound in the sediment would be 0.1/10 = 0.01 /yr with a half-life of 69 years.

EXAMS was designed for evaluative purposes, rather than for detailed site-specific applications. For this reason, EXAMS' transport algorithms were written in a very general form that uses an input description of the transport conditions in the system, rather than attempting to compute hydraulics and solids transport from first principles. Several cautions to the user defining an ecosystem for entry to the program are therefore in order.

First, because EXAMS is a compartment model, the representation of advected flows necessarily introduces some numerical dispersion into the computations. Although this poses little problem for general evaluations, it should be recognized that the concentrations computed by the program for a particular location are to a degree dependent on the spatial resolution used to represent the system. For example, EXAMS computes the average concentrations in a river reach, rather than the details of the (usually decreasing) profile of concentrations within the reach. As the number of compartments used to describe the reach increases, the compartmentalized representation begins to approach the more detailed profile predictable from an analytic solution to the governing partial differential equations. In general, for site-specific applications simplified transport representations can be adjusted or "calibrated" to more faithfully depict transport detail, via initial matching of program outputs to a conservative tracer substance. Chloride concentration is often used as a calibration tracer in estuaries; temperature and dissolved substances can be used for calibration studies in lacustrine systems. Of course, if desired, EXAMS could be loaded via an analysis of the outputs of detailed hydraulic and sediment transport models.

Secondly, EXAMS does not impose a segment-by-segment mass balance on the solid phases (sediments and biota) that transport sorbed chemicals through the system. In some instances, sediment (detrital materials) and biota are subject to significant creation and destruction in some areas of aquatic systems, so that, unlike water, these quantities cannot be treated as simple mass-conservative entities in a generalized algorithm. Thus, for example, mass balances for suspended sediments in EXAMS are left to the user's discretion. The EXAMS program, however, does not permit a failure to conserve sediment mass to perturb the mass balance for synthetic organic chemicals.

Exchanges with sediment beds are described primarily via a dispersive exchange term (Section 2.3.1.4). This approach involves a statistical summary of a multitude of physical and biological transport mechanisms that have not been fully characterized in the literature. It has disadvantages in that the appropriate magnitudes for the input parameters (e.g., DSPG) are only approximately known. Unfortunately, the magnitudes of the descriptive parameters needed for a more mechanistic characterization of these multiple physical and biological transport pathways are still less perfectly known. In general, the sensitivity of EXAMS' outputs to variation in sediment-water column exchange parameters should probably be routinely examined, at least for extensively sorbed compounds.

2.3.1.1 Hydrology and advection

Hydrologic inputs are specified in EXAMS' environmental data base via four variables: STFLOG (stream flow), NPSFLG (non-point-source flow), INTFLG (ground-water inflows), and RAING (rainfall). After subtracting evaporative water losses (EVAPG), the sum of these terms is the total water flow entering a compartment from external sources. EXAMS adds to this sum the advected flows entering the compartment via other compartments in the system. This grand sum is the total amount of water advected into the compartment from all (internal and external) sources combined. The total advective flow through the compartment is then distributed among the flow paths specified for that compartment in the JFRADG and ITOADG structural vectors.

Three of the hydrologic input variables (STFLOG, NPSFLOG, and INTFLG) are vectors that include a separate entry for each compartment of the aquatic system described by the data base. The STFLOG vector is used to enter point sources, tributary flows, stream flows entering a lake, and the discharge entering the uppermost reach of a river system. The NPSFLGs are used to enter non-point-flows and overland runoff flowing into the compartments. Ground-water seepage or subsurface flows are entered via INTFLG. STFLOG, NPSFLG, and INTFLG all have units of cubic meters per hour; EXAMS allows each compartment to receive an entry from each category.

Rainfall (RAING) is a scalar variable in EXAMS, that is, the environmental descriptor is a single value rather than a compartment-specific vector. RAING has units of mm/month. EXAMS converts this climatological datum to a quantity of water entering each compartment having an air-water interface. The conversion is simply:

Eq. 2.70 $$RAINFL = (RAING)(AREAG)/(730.5)$$

where RAINFL is in liters/hour (based on 730.5 hours/month). EXAMS detects the air-water interface, and decides whether to admit rainfall into the compartment, from the structure of the system. Rainfall is not permitted to enter compartment types (TYPEE) "B" (benthic) or "H" (hypolimnion). The decision mechanism for L(ittoral) and E(pilimnion) compartments is slightly more complex. For these compartment types, EXAMS checks the compartment numbered one less than the compartment under consideration (that is, if the current compartment is J, the decision is based on the properties of compartment (J-1)). If the preceding compartment is another element of the water column, rainfall is not allowed to enter the current (Jth) compartment.

At first glance, this decision seems trivial: after all, rain only falls on the water surface, therefore only these compartments can receive rainfall. The problem is complicated, however, by the fact that EXAMS was designed to allow a user to interactively modify any variable in the environmental data base. EXAMS therefore must be able to detect any change in the system structure and accurately recompute, in this case, a new hydrologic regime. Changes in system structure affect a number of other processes as well. For example, in computing vertical light extinction through the water column, EXAMS must detect the top of the water column, compute the light levels in each successively deeper water-column compartment, and then restart the computation for each adjacent vertical section.

The problem, then, is somewhat more general than it first appears, and is not entirely trivial: EXAMS must decode the three-dimensional structure of the system as an implicit function of the input environmental data. The decoded structure then serves as a guide for computing the kinetics of the transport and transformation processes. The decoding problem could, of course, be eliminated by requiring that the environmental data include a more complete set of structural descriptors. This approach, however, leaves the user in the uncomfortable position of having to memorize a large set of arbitrary, model-specific compartment descriptors of little intrinsic interest.

EXAMS instead relies on a set of simple conventions for numbering and naming the compartments used to describe an aquatic system. These conventions can be stated as 4 definition rules:

(1) Compartments can be named (TYPEE) either "L" (littoral), "E" (epilimnion), "H" (hypolimnion), or "B" (benthic). These names carry their usual implications: an "H" compartment lacks an air-water interface, a "B" compartment is a bottom sediment, etc. The water column of the littoral cannot be subdivided; all other system zones can be entered as vertical stacks of the same TYPEE.

(2) Compartment number 1 must be part of a water column and must be of TYPEE "E" or "L".

(3) Each vertical segment must be numbered in increasing order with increasing depth. That is, when a vertical segment is divided into, say, 4 compartments, if the topmost compartment is numbered 5, the bottom compartment will be number 8.

(4) Every vertical segment must terminate in at least one bottom sediment ("B") compartment.

EXAMS' computations are somewhat more efficient if one more rule is observed:

(5) Vertical blocks of compartments are arranged, and numbered, along the main advective flow paths in the system.

EXAMS' internal decoding of the (implied) system structure thus avoids the problem of multiple model-specific parameters, but at some cost: EXAMS must assume that the user has scrupulously adhered to these rules. Suppose, for example, that a 10-mile stretch of river were described as 10 successive "L" compartments, and the benthic sediments were omitted: EXAMS would suppose the system to be a vertical, 10-mile-deep column of water. Again, should a surface-water compartment be designated "H", EXAMS will not allow rain to fall, nor chemicals to volatilize, from the compartment. Examples of proper and improper segmentations of a small river and lake system are given in Figure 2.1.

a. Improper segmentation and numbering: compartment number 1 is (B)enthic, benthic sediments are incomplete, and numbering is horizontally rather than vertically organized.

```
    +-------------+    +---------+    +---------+    +-------------+
--->| 2         L |--->|         |--->|         |--->| 5         L |---->
    +-------------+    |         |    |         |    +-------------+
           ^           | 3     L |    |         |           ^
           |           +---------+    | 4     E |           |
           v                          +---------+           v
    +-------------+                        ^         +-------------+
    | 1         B |                        |         | 7         B |
    +-------------+                        v         +-------------+
                                      +---------+
^                                     |         |
|  is vertical exchange               |         |
v                                     |         |
                                      | 6     H |
                                      +---------+
                                           ^
                                           |
                                           v
                                      +---------+
                                      | 8     B |
                                      +---------+
```

b. Proper segmentation: vertically organized numbering, all vertical segments include a bottom sediment, and compartment number 1 is of surface water type ("L" or "E").

```
    +-------------+    +---------+    +---------+    +-------------+
--->| 1         L |--->|         |--->|         |--->| 8         L |---->
    +-------------+    |         |    |         |    +-------------+
           ^           | 3     L |    |         |           ^
           |           +---------+    | 5     E |           |
           v                ^         +---------+           v
    +-------------+         |              ^         +-------------+
    | 2         B |         v              |         | 9         B |
    +-------------+    +---------+         v         +-------------+
                       | 4     B |    +---------+
                       +---------+    |         |
^                                     |         |
|  is vertical exchange               |         |
v                                     | 6     H |
                                      +---------+
                                           ^
                                           |
                                           v
                                      +---------+
                                      | 7     B |
                                      +---------+
```

Figure 2.1 Example of compartmental system structure.

EXAMS' final hydrological input quantity is a compartment-specific vector of evaporative water loss rates, EVAPG, with units (mm/month). A value of EVAPG can be entered for any compartment, but EXAMS ignores inappropriate entries, that is, evaporation is allowed only for compartments with an air-water interface.

EXAMS can be operated with very generalized descriptions of aquatic systems typical of broad geographic regions, or with more detailed descriptions of particular sites and locales. The mechanics of EXAMS' transport computations can best be appreciated via a specific example. This example will be developed in considerable (site-specific) detail, so as to illustrate methods for preparing environmental data for EXAMS, computational mechanics, and the range of transport processes that can be accommodated by the program.

2.3.1.2 Advected water flows

EXAMS' advective flow computations are fundamentally nothing more than a direct application of the law of conservation of mass. Because changes in storage volumes are not permitted, the total inputs to each compartment must be balanced by advected outflows. The advective transport regime thus can be computed by imposing a water (mass) balance on the hydrologic inputs to the system. The logic of these computations can best be seen within the context of a specific example:

Figure 2.2 is a 9-compartment model of a portion of a slowly moving slough or river system. Upstream discharge into compartment 1 is 10 cubic meters/hr. The flow is split by an island into compartments 3 and 5; 75% of the flow goes to compartment 3, the remainder to compartment 5. Compartment 3 also receives a tributary discharge of an additional 10 cubic meters/hour. Each segment is 100 m long and 2 m deep. The segment widths are 10 m for 1 and 7, but compartment 3 is 8 m, and compartment 5 is 2 m, wide. The rate of evaporative water loss (EVAPG) is 146.1 mm/mo for all segments; no rain falls on the system. EXAMS' hydrologic input data, thus far, looks like this:

COMP.	STFLOG	AREAG	EVAPG	VOLG	DEPTHG
1	10	1000	146.1	2000	2
3	10	800	146.1	1600	2
5		200	146.1	400	2
7		1000	146.1	2000	2

EXAMS now converts STFLOG and EVAPG (via AREAG, as in Eq. 2.70) to the net liters/hour entering each compartment from external sources (WATINL), and sums the total available flow (TOTIN), arriving at the hydrologic analysis shown in Table 2.1.

```
                            |
                         10 |
                            |
                            V
                         +---------+
                         |         |
                       ->| 3     L |\
                      /  |         | \
                     /   +---------+  \
                    /    +---------+   \
    +---------+    /     | 4     B |    \    +---------+
    |         |   /      +---------+     \   |         |
--->| 1     L |--<                        >->| 7     L |---->
10  |         |  \                       /   |         |
    +---------+   \                     /    +---------+
    +---------+    \                   /     +---------+
    | 2     B |     \    +---------+  /      | 8     B |
    +---------+      \   |         | /       +---------+
                       ->| 5     L |/        +---------+
                         |         |         | 9     B |
                         +---------+         +---------+
                         +---------+
                         | 6     B |
                         +---------+
```

Figure 2.2 Nine-compartment model of Noname Slough ecosystem.

Table 2.1. Advective inputs to Noname Slough

COMP.	STRMFL	EVAPL	WATINL
1	10000	200	9800
3	10000	160	9840
5	0	40	- 40
7	0	200	- 200

		TOTIN =	19400

The structure of the advective flow field is given by parameters JFRADG, ITOADG, and ADVPRG. These names are acronyms for J FRom ADvection (JFRADG), I TO ADvection (ITOADG), and ADvection PRoportion (ADVPRG), respectively. (The terminal "G" merely indicates that these are "Global" parameters, that is, they are available to the user for interactive modification.) Vector JFRADG is a list of the source compartments for each flow. The corresponding member of ITOADG holds the number of the compartment receiving the flow, and ADVPRG gives the fraction of the total flow through compartment JFRADG that follows the path to ITOADG. A zero (0) entered in ITOADG denotes an export from the system. EXAMS' report of the (partial) structure given for the slough system in Figure 2.2 would appear as in Table 2.2.

Table 2.2. EXAMS output -- partial advective structure, Noname Slough.

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Unspecified Chemical
ECOSYSTEM: Noname Slough - Advection test data
---------------------------------------------------------------------------
TABLE 7.  INPUT DATA DESCRIBING ENVIRONMENT: ADVECTIVE INTERCONNECTIONS.
---------------------------------------------------------------------------
COMP. NO. (JFRAD)      1          1          3          5          7
CONNECTED (ITOAD)      3          5          7          7          0
ADVECTION (ADVPR) 0.750      0.250       1.00       1.00       1.00
```

EXAMS now combines the information given in Tables 2.1 and 2.2 into a set of input/output equations reflecting the conservation of water mass in the system. If X(I) denotes the total output flow from compartment (I), these equations can be written as:

```
OUTPUT  =            SUM OF INPUTS
------    -------------------------------------
 X(1)   =  9800
 X(3)   =  9840 + 0.75 X(1)
 X(5)   =   -40 + 0.25 X(1)
 X(7)   =  -200                 + 1.0 X(3) + 1.0 X(5)
```

This is a set of 4 simultaneous equations in 4 unknowns; it can be solved by successive elimination of terms in the usual way. In this case, it is easy to see that:

```
        X(1)                          =  9800
        X(3) = 9840 + 0.75(9800)      = 17190
        X(5) =  -40 + 0.25(9800)      =  2410
and     X(7) = -200 + 17190 + 2410    = 19400
```

EXAMS was written to accommodate N equations in N unknowns. In other words, the program solves the input/output advective equations for an arbitrary number (N) of compartments, any of which can receive, deliver, or exchange advected flows with any or all of the other compartments in the system. The N input/output equations are solved by a Gaussian elimination algorithm (Stuart 1970:304-311). This algorithm is a matrix solution of a normalized form of the input/output equations. The matrix (AMAT) is loaded in three stages: First, each value of WATINL is divided (normalized) by TOTIN, and loaded on the (N+1) column of AMAT. Next, the coefficients on the output (X) terms (which are always unity (1)) are loaded on the diagonal of AMAT. Finally, the ADVPR values are entered into AMAT with a row index given by ITOADG and a column index given by JFRADG. (The system export terms (ITOADG = 0) are not required for this part of the analysis.) Leaving aside Noname Slough's benthic compartments, the coefficient matrix would be:

Table 2.3. Normalized coefficient matrix, advection equations

	JFRAD				
ITOAD	1	3	5	7	WATFL/TOTIN
1	1	0	0	0	0.505155
3	-.75	1	0	0	0.507216
5	-.25	0	1	0	-0.002062
7	0	-1.0	-1.0	1	-0.010309

The solution of this system of equations is:

X(1) = 0.505155
X(3) = 0.886082
X(5) = 0.124227
X(7) = 1.000000

where "X" is now the fraction of TOTIN passing through each compartment.

For each compartment, EXAMS computes the actual discharges along each flow path as the product of X, TOTIN, and the ADVPRG for the pathway. This information is entered in a matrix (WATFL) of flows among segments. The row and column indices of WATFL are the same as those of AMAT, that is, the WATFL indices give the source and destination compartment number for each flow. Exports from the system (in liters per hour) are entered into a vector (WATOUL) of exports from each compartment. The exports from each (JFRADG) compartment are computed as the product of X, TOTIN, and ADVPRG for those pathways having ITOADG = 0.

In the Noname Slough example, the discharges from segment number 1 are:

WATFL(3,1) = (0.505155)(19400)(0.75) = 7350,

and

WATFL(5,1) = (0.505155)(19400)(0.25) = 2450.

The only non-zero outlet flow is

WATOUL(7) = (1.0)(19400)(1.0) = 19400.

The WATFL matrix and the WATOUL vector for these sections of Noname Slough are shown in Table 2.4. EXAMS' outputs include a "transport profile" of the system, showing the advected flows through each segment. EXAMS also computes a (local) turnover or "water renewal" time (the volume/discharge ratio) for each compartment. EXAMS' transport profile for Noname Slough, as defined thus far, is given in Table 2.5.

Table 2.4. Example WATFL matrix and WATOUL vector (liters/hour)

		JFRAD			
		1	3	5	7
ITOAD	1	0	0	0	0
	3	7350	0	0	0
	5	2450	0	0	0
	7	0	17190	2410	0
WATOUL:		0	0	0	19400

Table 2.5. Partial transport profile for Noname Slough

```
 AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Unspecified Chemical
ECOSYSTEM: Noname Slough - Advection test data
------------------------------------------------------------------------------
TABLE 9.  TRANSPORT PROFILE OF ECOSYSTEM.
------------------------------------------------------------------------------
CP T*   VOLUME     SEDIMENT  WATER FLOW  SED. FLOW  RESIDENCE TIME (DAYS)
   Y   (CUBIC M)   MASS (KG) (CU. M/DAY) (KG/DAY)      WATER    SEDIMENTS
------------------------------------------------------------------------------
  1L   2.0000E+03              235.                    8.50
  2B
  3L   1.600E+03               413.                    3.88
  4B
  5L    400.                   57.8                    6.92
  6B
  7L   2.000E+03               466.                    4.30
  8B
  9B
------------------------------------------------------------------------------
* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC
```

2.3.1.3 Advective sediment transport

Sedimentary materials (detritus) can be produced and destroyed biogenically within an aquatic ecosystem. Sediment transport thus is not computed in EXAMS via the simple mass balance constraints used to compute the transport of advected water masses. EXAMS instead treats advected sediment as a non-conservative substance whose transport is simply driven by the hydrodynamics of the system. The point- (STFLOG) and non-point- (NPSFLG) external hydrologic inputs do contain coupled sediment loads (STSEDG and NPSEDG, kg/hr). These variables are only used, however, to evaluate the chemical loadings (see Section 2.4); they do not enter the chemical transport equations.

EXAMS computes advective sediment transport as the product of the rates of water transport and the sediment/water ratio (SEDCOL, Eq. 2.12) of the source compartments. WATFL and WATOUL are used to load an analogous sediment flow matrix (SEDFL) and export vector (SEDOUL), both having units of kg sediment transported per hour. The equation for advective sediment transport among compartments is:

Eq. 2.71 $$SEDFL(I,J) = WATFL(I,J) * SEDCOL(J),$$

and the equation for advected sediment export is

Eq. 2.72 SEDOUL(J) = WATOUL(J) * SEDCOL(J).

These equations are not blindly executed for the entire system, however.

The execution of the sediment transport equations (Eqs. 2.71 and 2.72) is constrained by a series of special conditions. These conditions can be expressed as a set of 5 sediment transport rules:

(1) An advected water mass leaving any water column compartment carries an entrained sediment washload, unless the flow enters a benthic compartment. A flow from the water column into a benthic sediment is an infiltration flow that does not transport sediments.

(2) Benthic sediment ("B") compartments can always export water across system boundaries, and can advect water to any other compartment in the system.

(3) A benthic compartment can export sediment (in addition to water) only when it occupies the sediment-water interface (that is, the (J-1) compartment is not of TYPEE "B").

(4) Sediment cannot be advected from a benthic compartment to any element of the water column.

(5) When benthic compartments are not vertically adjacent (actually, when their compartment numbers differ by 2 or more), sediments can be advected from one to another (for example, along a bedload transport path).

These sediment transport rules allow EXAMS to include sediment washloads and bedloads, and seepage of groundwater both into and out of the system. One additional system definition rule must be observed, however, when a groundwater recharge is portrayed: The groundwater flow path must include at least 2 vertical benthic sediment compartments. If this definition rule is ignored, EXAMS will interpret the export flow leaving the benthic compartment as a bedload (rule 3) rather than as a groundwater recharge.

These concepts can be illustrated by expanding the definition of Noname Slough (Figure 2.3). In the expanded definition, one segment receives a groundwater input (INTFLG) of 0.2 cubic meters/hour. The groundwater seep passes through benthic compartment 6 and is advected into the overlying water (rule 2); by rule 4 the water flow does not entrain a sediment flow. The downstream segment (7) loses water to a groundwater recharge. The infiltration flow is 2% of the total advected flow through compartment 7 (ADVPRG = 0.02). By rule 1, the infiltraton does not entrain the suspended sediments. The groundwater recharge must be carried on from compartment 8 into compartment 9 before it can be exported from the system, however, or EXAMS would interpret the export as a bedload (rule 3) rather than as a flow of water only (rule 2). The bedload path (compartment 2 to 4 to 8), by rule 5, carries both water and sediments downstream. The bedload export at compartment 8 is enabled under rule 3. The washload (compartments 1 to 3, 5 to 7) moves through the system under rule 1; EXAMS computes the downstream transport of suspended sediment from Eq. 2.71.

```
                             |
                          10 |
                             |
                             V
                          +---------+
                          |         |
                        ->| 3     L |\
                       /  |         | \
                      /   +---------+  \
                     /    +---------+   \
    +---------+     /   ->| 4     B |\   \    +---------+
    |         |    /   /  +---------+ \   \   |         |
--->| 1     L |--<    /                \   >->| 7     L |---->
10  |         |    \ /                  \ /   |         |
    +---------+     X                    X    +---------+
    +---------+    / \                  / \   +---------+
--->| 2     B |---    \   +---------+  /   -->| 8     B |---->
    +---------+        \  |         | /       +---------+
                        ->| 5     L |/        +---------+
                          |         |         | 9     B |
                          +---------+         +---------+
                          +---------+             |
                     ---->| 6     B |             | 2%
                    0.2   +---------+             V
```

Fig. 2.3 Noname Slough bedload, washload, and groundwater flows.

To complete this example, some additional properties of the sediments must be specified. Let, therefore, Noname Slough have a suspended sediment concentration (washload, SDCHRG) of 100 ppm, and stream-borne sediment loadings (STSEDG(1) and (3)) of 1.0 kg/hr. (Note that this treatment imposes a mass balance on suspended sediments.) The depth of the surficial sediments (compartments 2, 4, 6, and 8) is 5 cm; each has a bulk density (SDCHRG) of 1.2 g/cc, and a water content (PCTWAG) of 180%. Segment 9 is a 30 cm layer of sand with a bulk density of 1.95 g/cc, and a water content of 115%.

The bedload is, of course, another measurable property of the Slough. Suppose, for example, the measured bedload leaving the downstream segment of the Slough were 100 kg/hr. The ADVPRG for the crossed infiltration and bedload transport through compartment 8, and the upstream bedload inputs, can be developed from this datum and an assumed solids balance for the system.

The sediment/water ratio for the surficial sediments is 1.25 kg/liter (Eq. 2.13); the water export associated with the bedload is, therefore, (100)/(1.25) = 80 liters per hour = 0.08 cubic meters/hr. The groundwater infiltration was given as 2% of the available discharge passing through segment 7 (Figure 2.3). The total segment 7 discharge is 19.4 cubic m/hr (Table 2.4), plus the groundwater seep entering via segment 6 (Figure 2.3), or 19.6 cubic meters/hour. The 2% infiltration is therefore (0.02)(19.6) = 0.392 cubic m/hr, and the total flow through compartment 8 is 0.392 + 0.08 = 0.472 cubic m/hr. The ADVPRG for the throughput of infiltrated water is therefore (0.392)/(0.472) = 0.83; the ADVPRG for the bedload is 0.17.

Finally, presuming the bedload originates in equal measure from the influent flows to compartments 2 and 4, the bedload inflows to both segments are 0.04 cubic meters of water per hour (STFLOG(2) and (4)), with a parallel sediment load (STSEDG) of 50 kg/hr. EXAMS' retrieval of the full advective specifications is shown in Table 2.6, and EXAMS' computed advective "transport profile" is reprinted in Table 2.7.

Table 2.6. Full advective structure of Noname Slough

```
 AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Unspecified Chemical
ECOSYSTEM: Noname Slough - Advective transport regime
---------------------------------------------------------------------------
TABLE 8.  INPUT DATA DESCRIBING ENVIRONMENT: TURBULENT INTERCONNECTIONS.
---------------------------------------------------------------------------
COMP. NO. (JFRAD)      1          1          3          5          7
CONNECTED (ITOAD)      3          5          7          7          0
ADVECTION (ADVPR) 0.750      0.250       1.00       1.00      0.980
COMP. NO. (JFRAD)      7          2          4          6          9
CONNECTED (ITOAD)      8          4          8          5          0
ADVECTION (ADVPR) 2.000E-02   1.00       1.00       1.00       1.00
COMP. NO. (JFRAD)      8          8
CONNECTED (ITOAD)      9          0
ADVECTION (ADVPR) 0.830      0.170
```

Table 2.7. Advective transport regime in Noname Slough

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Unspecified Chemical
ECOSYSTEM: Noname Slough - Advective transport regime
-------------------------------------------------------------------------
TABLE 9.  TRANSPORT PROFILE OF ECOSYSTEM.
-------------------------------------------------------------------------
CP T*   VOLUME     SEDIMENT  WATER FLOW  SED. FLOW   RESIDENCE TIME (DAYS)
   Y  (CUBIC M)  MASS (KG) (CU. M/DAY) (KG/DAY)      WATER    SEDIMENTS
-------------------------------------------------------------------------
  1L  2.000E+03   200.        235.        23.5       8.50        8.50
  2B   50.0      3.333E+04  0.960       1.200E+03   27.8        27.8
  3L  1.600E+03   160.        413.        41.3       3.88        3.88
  4B   40.0      2.667E+04   1.92       2.400E+03   11.1        11.1
  5L   400.       40.0       62.6         6.26      6.39        6.39
  6B   10.0      6.667E+03   4.80       0.000       1.11
  7L  2.000E+03   200.       470.         46.1      4.25        4.34
  8B   50.0      3.333E+04   11.3       2.407E+03   2.35        13.8
  9B   300.      5.087E+05   9.40       0.000       8.12
-------------------------------------------------------------------------
* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC
```

2.3.1.4 Dispersive transport

The mean advected flow is not the only process governing the transport of synthetic chemicals in aquatic systems. Turbulence and shear flow in rivers, for example, combine to generate a wide spectrum of meso-scale advective processes. Similarly, in stratified lakes exchange across the thermocline is driven by molecular diffusion, wind-induced mixing, storm surges, and internal waves and seiches. These meso-scale processes can usually be described via a statistical summary (the dispersion equation) of their effects on the average transport of dissolved substances (see, for example, Fischer et al. 1979). EXAMS' environmental data base includes 5 vectors that specify the direction (JTURBG, ITURBG), and strength (DSPG, XSTURG, CHARLG) of dispersive transport pathways in an aquatic system.

The corresponding members of the JTURBG and ITURBG vectors specify the pair of compartments that are exchanging materials via each dispersion pathway. For example, the 4th entry in the vectors could be used to specify an exchange between compartments 7 and 10, by setting JTURBG(4) = 7, and ITURBG(4) = 10. Because dispersion, unlike advection, is a symmetrical process, this pathway could also be specified as JTURBG(4) = 10 and ITURBG(4) = 7. Boundary conditions (dispersive exchanges with the external world) are specified by a 0 setting on either vector. In other words, the vectors can specify a turbulent exchange of, for example, compartment 10 (an embayment), with an external reservoir, via either (JTURBG = 10; ITURBG = 0) or (JTURBG = 0;

ITURBG = 10). EXAMS computes the boundary exchanges as a simple displacement of contaminated, by chemical-free, water and sediments. Non-zero chemical boundary conditions are loadings, and thus would interfere with EXAMS' estimates of persistence (defined as the time to cleanse the system after all loadings terminate). Non-zero (dispersive) chemical boundary conditions can, of course, always be introduced via an artificial point-source or non-point-source advective input, coupled with a symmetrical advective export from the compartment, or via a DRFLDG (see Section 2.4).

The conventional dispersion equation used in EXAMS describes the rate of exchange of environmental volume across a boundary between two compartments. EXAMS' formula is:

Eq. 2.73
$$F = \frac{(\mathrm{DSPG})(\mathrm{XSTURG})}{(\mathrm{CHARLG})}$$

In this equation, XSTURG is the cross-sectional area of the pathway (in square meters), CHARLG is the "characteristic length" of the path (m), and DSPG is the dispersion coefficient or eddy diffusivity (square meters/hour). F is then a flow of environmental volume, with dimensions of cubic meters per hour. Equation 2.73 is homologous with the mathematics of simple Fickian molecular diffusion. The dispersion equation, however, is a statistical summary of the large-scale effects of meso-scale advective processes; it is used when the meso-scale processes are so complex or sporadic that a detailed treatment is intractable. The net result of the meso-scale processes is similar to molecular diffusion in that dissolved constituents are transported along the gradients of concentration in the system. The apparent rate of transport of materials from areas of high, to areas of low, concentration is much faster than rates of molecular diffusion, however. For this reason, the kinetic parameter in Eq. 2.73 (DSPG) is usually called a "dispersion coefficient," "turbulent diffusivity,", or "eddy diffusivity," rather than a "diffusion" constant (Bird, Stewart, and Lightfoot 1960:629). The events described by dispersion are not fully homologous with Fickian diffusion, however, and the use of dispersion terms to depict chemical transport in sediments requires careful adjustment for effects of porosity, tortuosity, sorption, and ion exchange (Berner 1976).

From the dispersion equation (2.73), EXAMS computes a flux of water and sediments along the pathway specified by JTURBG and ITURBG. The fluxes between compartments are added to the advective flows in matrices WATFL and SEDFL, thereby completing EXAMS' description of the system's internal flow field. The boundary fluxes are added to the appropriate elements of WATOUL and SEDOUL; the exchange brings in a replacement volume of uncontaminated water and sediments.

The "characteristic length" (CHARLG) of a pathway conventionally represents the distance between compartment centers, measured along the axis of the exchange. A single segment thus may have several characteristic lengths, depending on the geometric orientation of its linkages to adjoining segments. The cross-sectional area (XSTURG) for the exchange path also depends upon the orientation of the compartments. For a vertical exchange, as for example transport across the thermocline of a lake, XSTURG is usually the AREAG of the hypolimnion compartment. Longitudinal dispersion in a river conventionally takes the flow cross section as XSTURG, however, and this does not correspond to any value of AREAG. Adherence to these conventions is left to the user's discretion. EXAMS does not attempt to evaluate the geometry of the system, but simply inserts the user's entries for CHARLG and XSTURG into Eq. 2.73.

Although EXAMS does not evaluate the orientation of the dispersive exchange pathways, the program does adjust its computations according to the nature (that is, the TYPEE) of the exchanging compartments. These adjustments are primarily important for the exchanges across the benthic boundary layer, because of the very different physical properties of the water column and a sediment bed. In this case, a simple symmetric exchange of environmental volumes would transport very different sediment masses and volumes of water. EXAMS allows for the possibility of biogenic production and decay of detrital sedimentary materials, and thus generally does not impose explicit internal mass-balance constraints on the transport of sediments in the system. In this case, however, the massive injection of bed sediments into the water column, with little or no resettlement, would amount to a gross distortion of sediment transport dynamics beyond the realm of biogenic possibility. The simple dispersion equation (2.73) thus requires situational adjustments. EXAMS therefore divides its dispersion computations into 3 distinct cases: (1) dispersion between water column compartments, (2) dispersion between benthic compartments, and (3) dispersion between a benthic sediment and the overlying water column.

(1) Dispersion within the water column:

The volumetric displacement of suspended sediments can almost always be neglected, so the water volumes and environmental volumes of water column compartments can be assumed not to differ. For example, a 15000 mg/L washload with a density of 1.5 g/cc would perturb this assumption by only 1%. EXAMS therefore computes the exchange flow of water between water-column compartments (in liters/hour) as:

Eq. 2.74 $$\mathrm{FLOW} = \frac{(1000)(\mathrm{DSPG})(\mathrm{XSTURG})}{(\mathrm{CHARLG})}$$

This value is added to the advective flows already in WATFL(I,J) and WATFL(J,I). (I is the compartment number held in ITURBG; J is the compartment number held in JTURBG.) The dispersive exchange is equivalent to a symmetric pair of advected (pseudo) flows between the compartments. If FLOW is a boundary condition, it is added to WATOUL(J), where J is the compartment number held by the non-zero member of the (JTURBG, ITURBG) couple.

The SEDFL matrix is updated via

Eq. 2.75   SEDFL(I,J) <--- SEDFL(I,J) + (FLOW)*(SEDCOL(J))

and

Eq. 2.76   SEDFL(J,I) <--- SEDFL(J,I) + (FLOW)*(SEDCOL(I))

The SEDOUL vector is updated via

Eq. 2.77   SEDOUL(J) <--- SEDOUL(J) + (FLOW)*(SEDCOL(J))

(SEDCOL is the sediment/water ratio, Eq. 2.13). In this case, sediment mass need not be conserved. When the exchanging compartments have differing concentrations of suspended sediments, EXAMS permits a net flow of sediments along the concentration gradient. EXAMS assumes that biogenic production and decay of detrital materials within the compartments serves to maintain the gradient.

EXAMS computes lateral, vertical, and horizontal dispersion via this procedure. The equations thus account for several rather different processes. The effects of shear flow in rivers are computed via a "longitudinal dispersion coefficient." Depending upon the geometry and slope of the channel, riverine longitudinal dispersion coefficients can vary from 2700 (Yuma Mesa A Canal, Schuster 1965) to 5.4E6 (Missouri River near Blair, Nebraska; Yotsukura et al. 1970) square meters per hour (cited from Fischer et al. 1979:126). Some small lakes develop nearly uniform vertical density gradients that inhibit vertical exchange, while allowing rapid lateral dispersion, at all depths in the lake. Usually, however, the most important barrier to vertical transport in lakes is a localized region (the metalimnion or thermocline) with a steep temperature (density) gradient. The exchange of epilimnetic and hypolimnetic water masses is driven by wind-induced eddies, storm surges, and internal seiches (see, for example, Wetzel 1975:89-122). The net effect of these processes can usually be summarized via a dispersion equation. For example, Snodgrass (1977) used a "vertical diffusivity coefficient" to "integrate the effects of molecular diffusion, eddy diffusion, internal waves, seiches, standing waves, [and] hypolimnetic entrainment . . . into a net transport process" across the thermocline of Lake Ontario. The average DSPG during the stratified period (April to November) ranged from 1.0 to 4.1 square meters per day, over 6 years of measurements.

(2) Dispersion within the bottom sediments:

In some cases, exchanges among benthic compartments require adjustment for strongly differing properties of the exchanging segments. The surficial sediments of Noname Slough (Figure 2.3) are laterally homogeneous, for example, but the deeper sandy layer (compartment 9) differs substantially from the surficial layers in bulk density, water content, and organic carbon content. The sediment/water ratios of these layers can be compared by inserting their water contents (PCTWAG) into Eq. 2.13. In the surficial sediments, the given water content is 180%, and SEDCOL = 1.25 kg sediment per liter of water. The sandy layer has a water content of 115%; its SEDCOL (6.67 kg/liter) is 5 times that of the surficial layers. Dispersion between benthic compartments therefore must allow for exchanges between segments of very different physical properties.

Furthermore, the water volume and the environmental volume of a benthic sediment are by no means the same. The surficial sediments of Noname Slough, to continue the example, have a given bulk density of 1.2 g/cc. The volumetric (liter/liter) water content ("porosity") can be computed via Eq. 2.12-2.12.3; the surficial sediments contain only 0.53 liters of water per liter of environmental volume. The porosity of the sandy layer (bulk density 1.95 g/cc) is only 0.25 L/L. Equation 2.74 thus cannot be used for a direct computation of dispersive transport of a synthetic chemical between benthic sediment compartments.

The distribution of chemicals within lacustrine and marine sediments has been successfully modeled via a vertical one-dimensional treatment of transport and chemical dynamics in this subsystem (Berner 1976, Imboden and Lerman 1978, Jones and Bowser 1978). These one-dimensional ("diagenetic") equations include the usual dispersive, advective, and reaction terms. The advective terms in these equations are often used to describe the net deposition of sedimentary materials, and the effective vertical flow of interstitial waters produced by compaction of the deposits. EXAMS precludes deposition and permanent burial of synthetic organic chemicals as inappropriate to an evaluative model, so its advective terms (Section 2.3.1.3) represent ground-water flows and, where appropriate, irrigation of benthic deposits by burrowing organisms.

The activities of burrowing organisms (bioturbation), physical disturbance by demersal fishes, and intermittent strong water turbulence tend to physically mix solids deposited on the sediment surface to appreciable depths. These actively mixed zones generally extend from about 2, to as deep as 50, centimeters in natural systems (Jones and Bowser 1978 and references therein). This physical reworking modifies observed concentration profiles in sediments, and has led Schink and Guinasso (1977) to propose the use of explicit solids mixing terms in the one-dimensional treatment of early diagenesis in sediments.

EXAMS makes use of a compartmentalized realization of these one-dimensional equations, but does not permit explicit mixing of sediment solids between benthic compartments. The depth of the sediment compartments used to describe a system is taken to be a depth through which the sediment can be regarded as "well-mixed." The mixing of solids is thus implicity incorporated into the specifications of the structure of the system, rather than as direct terms in the simulation equations. In effect, therefore, EXAMS assumes that vertical concentration gradients within the benthic compartments do not greatly disturb the results of its evaluations.

There is some experimental evidence that the speed of internal mixing processes in surficial sediments is sufficiently rapid to justify EXAMS' discretized treatment. For example, McCall and Fisher (1977, quoted from Jones and Bowser 1978) have shown that typical population densities of tubificid oligochaetes can completely rework the top 5 cm of sediments every 2 weeks in a laboratory setting. Vanderborght and Wollast (1977) found that the upper 3 cm of marine (North Sea) sediments exhibited an internal dispersion coefficient of 1.E-4 square cm/sec; this value implies a reworking time of only 25 hours.

When a dispersion term (lateral or vertical) is specified for exchange between benthic compartments, EXAMS computes a symmetrical exchange of water (only) between the compartments. This exchange flow is used to update the WATFL matrix. Generally the input dispersion coefficient in such a case should be corrected only for tortuosity; the program itself corrects for the average porosity of the 2 compartments involved, and for sorption of the chemical to solid phases. EXAMS imposes no limitations on the magnitude of DSPG. Irrigation of deep sediment zones by burrowing organisms can thus be represented via dispersion terms, if desired. A boundary condition for a bottom sediment compartment is computed in much the same way, except, of course, the porosity of the specified compartment is the only datum available for correction of the nominal DSPG.

(3) Exchanges between bed sediments and overlying waters:

Capture of organic chemicals by sediment beds can occur via several processes. A dissolved phase can sorb directly to the surface of the bed, with the sorbed material being then subducted into the bed via bioturbation. Irrigation of the sediments by tube-dwelling animals can directly entrain a flow of contaminated water through the bed; the sediment solids will then tend to strip chemical from the water flow. Filter-feeding organisms can aggregate compounds sorbed with suspended fine particles and add material to the bed, as may the sequential deposition, internal mixing, and scour events characteristic of riverine systems. In lakes and oceans, sediment "bursting" (Heathershaw 1974) results in frequent saltation of bed solids, leading to sorption/desorption events and entrapment of free boundary waters in the redeposited sediment matrix.

Although direct sorption/desorption to the sediment surface is a continuous process, many of the interactions between the water column and benthic sediments are highly intermittent. For example, Heathershaw (1976) has estimated that, in well-mixed areas of the Irish Sea, as much as 70% of the Reynolds stress in the benthic boundary layer results from events occupying only 5% of the total time of record. Interactions mediated by the biota are presumably also intermittent and highly variable in their intensity. The most practical and efficient means of representing this array of interactions between the water column and benthic sediments is to use a statistical summary of their macro-scale effects, that is, a dispersion equation (Berner 1976). This strategy was adopted for EXAMS.

A dispersive exchange between a water column (L, E, or H) and a benthic (B) compartment is described to EXAMS via specification of a characteristic length (CHARLG), cross-sectional area (XSTURG), and dispersion coefficient (DSPG) for the water column -- benthic element exchange pathway. The volumetric exchange given by FLOW (Eq. 2.74) can be regarded (heuristically) as the saltation of a unit volume of the bed (containing water and solids), followed by equilibration with the water column and resettlement on the bed. EXAMS thus separates the rate of exchange of environmental volume given by (DSPG)(XSTURG)/(CHARLG) into distinct water and solids exchange components. The porosity of the benthic sediment is coupled to the dispersion equation to give a water-exchange term, via the expression:

$$\frac{\mathrm{WATVOL}}{\mathrm{VOLG}} * \frac{(\mathrm{DSPG})(\mathrm{XSTURG})}{\mathrm{CHARLG}}$$

This water flow term (units of liters/hour) is then used to update symmetric locations in the WATFL matrix, giving an apparent rate of exchange of fluids between the water column and the interstitial pore waters of the benthic sediment compartment. Chemical transport can then be computed by treating these water flows as simple carriers for the dissolved fraction resident on either side of the benthic boundary layer.

In some cases, exchanges across the benthic boundary layer can be treated as being driven by gradients in dissolved chemical concentrations alone. Many synthetic organic chemicals, however, have very high partition coefficients, so that sorption onto the surface of the bed followed by bioturbational subduction is probably a significant mechanism of chemical transport for these compounds. The remaining exchange volume is therefore taken to represent a direct interaction of the bed solids with the water column compartment. First, an apparent "resuspension" or "bursting" term for the exposure of the bed solids to the water column is computed as the product of the sediment:water ratio (SEDCOL) of the benthic zone and the fluid exchange rate. The SEDFL matrix is thus updated by an apparent flow of bed sediments (TEMSED, units kg/hour) into the water column via the expression:

$$\text{Eq. 2.78} \qquad \text{TEMSED} = \text{SEDCOL} * \frac{\text{WATVOL}}{\text{VOLG}} * \frac{(\text{DSPG})(\text{XSTURG})}{\text{CHARLG}}$$

Strictly speaking, a "solids balance" now requires that an equal mass of sediment resettle on the bed, in order to maintain the notion of a stable (steady-state) bed thickness. The transport of a chemical across the benthic boundary layer can then be computed by regarding the solid phase as a simple carrier of sorbed chemicals, using sorbed concentrations (mg/kg solids) on either side of the boundary.

The foregoing is, for the most part, conventional compartment modeling. Still, because a multitude of processes have been summarized in a single kinetic expression, a careful independent trial of the approach seemed warranted. Although a number of experimental tests of the equations can be imagined, initial tests were conducted by comparing the output from the EXAMS program to a example situation constructed on theoretical grounds alone. This test was conducted on a reduced subsystem of the Noname Slough ecosystem. Consider, for example, the vertical segment of Noname Slough that includes a 2 m water column underlain by a 5 cm mud deposit and a 30 cm layer of sand (Figure 2.3). If the transport characteristics of this subsytem are redefined to eliminate the bedload and groundwater infiltration, the dispersion equation can be used to describe vertical movement of a chemical in the subsystem.

Retaining the physical sediment characteristics (SDCHRG, PCTWAG) developed in Section 2.3.1.3, the sorptive properties of the sediments must now also be specified. For the example, let the organic carbon content of the washload be 2% (FROCG = 0.02), that of the mud layer 5%, and let the sand contain only 0.1% organic carbon. The characteristic length (CHARLG) and exchange cross section (XSTURG) for the dispersive exchanges can in this instance be developed directly from the geometry of the system. These values, along with the kinetic exchange coefficients (DSPG) are given in Table 2.8. Vanderborght and Wollast (1977), working with rhodamine dye in North Sea sediments, found that physical turbulence induced benthic boundary layer exchange coefficients of 2.9E-6 to 6.2E-4 square cm/sec. The test DSPG for Noname Slough were selected from this range of values.

Table 2.8. Dispersive interconnections for Noname Slough test subsystem

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Unreactive test chemical: Koc = 3.E5
ECOSYSTEM: Noname Slough - Dispersion equation test data
-----------------------------------------------------------------------
TABLE 8.  INPUT DATA DESCRIBING ENVIRONMENT: TURBULENT INTERCONNECTIONS.

COMP. NO. (JTURB)        7           8
CONNECTED (ITURB)        8           9
X-SECTION (XSTUR)  1.000E+03   1.000E+03
CHAR. LN. (CHARL)   1.02        0.175
EDDY DISP. (DSP)   1.500E-04   3.600E-05
```

In order to test the dispersive transport alogorithm in isolation, the test chemical can be specified as a completely unreactive, non-volatile neutral compound, with a Koc of 3.E5.

When the test chemical is introduced into the system, an equilibrium state could be rapidly generated by suspending the benthic layers in the water column, and thoroughly agitating the mixture. At equilibrium, this 4-phase system would exhibit a single aqueous concentration, and sorbed-phase concentrations differing as the ratio of their partition coefficients (i.e., in proportion with the organic carbon contents of the sediment phases). If the bed solids were then allowed to resettle, the simple separation of the materials would not result in any change in the dissolved (mg/L of water) or sorbed (mg/kg dry solids) concentrations. The environmental concentrations (mg/L of total environmental volume) could, of course, differ between the water column and the (restored) bed layers.

This situation also applies to an open system in a dynamic equilibrium or steady state. Suppose, for example, that water contaminated to a level of 1 ug/L (ppb) with the test chemical flows continuously through the Noname Slough subsystem. The dispersion equation controls only the rate of exchange of chemical between the water column and the benthic subsystem. At steady state, no concentration gradient remains to drive further net chemical exchange. In this instance of an unreactive compound, the final dynamic equilibrium is equivalent to the static case.

The resulting computer output is shown in Table 2.9a. The computations lead to a steady-state end point of equal sorbed concentrations for the washload and the mud layer, rather than equal dissolved concentrations. Although the concentration distribution between the bed sand and mud layers follows the theoretical expectations, this result for the washload and the mudlayer is exactly opposite the expected outcome of the test.

Table 2.9a. EXAMS test of dispersive exchange equations.

```
   AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
 CHEMICAL: Unreactive neutral compound -- Koc = 3.E5
 ECOSYSTEM: Noname Slough -- Dispersion equation test data
 -------------------------------------------------------------------------
 TABLE 13. DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
 -------------------------------------------------------------------------
 COMP STEADY-STATE RESIDENT MASS      **** TOXICANT CONCENTRATIONS ****
         2                           TOTAL   DISSOLVED SEDIMENTS   BIOTA
      G/M       KILOS         %       MG/*     MG/L      MG/KG      UG/G
 --- ------    ------     ------   --------- --------- --------- ---------
   1 2.000E-03 2.0001E-03 100.00   1.000E-03 6.250E-04  3.75
  SUBTOTAL:    2.0001E-03   1.21
  AND IN THE BOTTOM SEDIMENTS:
   2 0.125     0.1250      76.61    3.75     2.500E-04  3.75
   3 3.818E-02 3.8176E-02  23.39   7.505E-02 2.500E-04 7.501E-02
  SUBTOTAL:    0.1632      98.79
 TOTAL MASS (KILOGRAMS) =    0.1652
 -------------------------------------------------------------------------
 * TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.
```

Although the computed outcome could be rationalized in many ways, the fact remains that the program output did not reflect the assumptions and reasoning used to build the model; it thus required revision.

Closer consideration of the heuristic logical structure used to adapt the dispersion equation to this application suggested an appropriate revision. At least nominally, in the case under consideration the suspended and bedded solids need never even come in contact, so there is no plausible way for sorbed chemical to experience a direct concentration gradient. The capture of chemical by the bed is driven by fluid exchange, and by saltation of the bed solids, which allows them to interact directly with chemical dissolved in the water column. The root of the problem thus seems to lie with the difference in organic carbon content (i.e., partition coefficient) of the suspended and bedded sediments.

The sorbed concentrations computed for each compartment are based on properties of the sediments specified for the compartment, rather than on the properties of a saltatory transient. Therefore, it might serve the case to simply adjust chemical transport according to the ratio of the partition coefficients (Kp). In this way, for example, if the Kp of the bed sediment were 5 times that of the suspended sediment, the rate of capture of chemical by the bed would be proportionally larger than that suggested by Eq. 2.78 simply coupled to the concentration on the washload, and conversely.

Although organic carbon content governs the ability of a sediment to sorb neutral (uncharged) molecules, an organic acid or base will occur as both neutral and charged species, with a speciation governed by the pH of the system. The sorptive capacity of a sediment may thus depend on its carbon content, ion exchange capacity, and the pH of the compartment. Thus when necessary, the relative sorptive capacity of sediment phases can be computed via the distribution coefficients (ALPHA) and sediment:water ratios (SEDCOL) of the water-column and benthic compartments specified for an exchange pathway. Given ALPHA(16,w) and ALPHA(16,b) as the total dissolved fraction in the water column (w) and benthic (b) compartments, respectively, and ALPHA(17,w) and (17,b) as the sediment-sorbed fractions, the return "flow" (SEDFL) of suspended sediment across the benthic boundary layer to the sediment compartment can be computed as:

$$\text{TEMSED} * \frac{\text{ALPHA(16,w)} * \text{SEDCOL(w)}}{\text{ALPHA(17,w)}} * \frac{\text{ALPHA(17,b)}}{\text{ALPHA(16,b)} * \text{SEDCOL(b)}}$$

This calculation yields the ratio of the sorptive capacity (overall partition coefficient, Kp) of the benthic sediment, to that of the washload. Thus for example, if the benthic sediments have a Kp twice that of the washload, the rate of capture of chemical by the bed (that is, the apparent pseudo-settlement rate of saltatory bed materials) must occur at twice the rate that would be inferred directly from the properties of the washload itself.

The effect of this revision can now be tested by execution of the test case described above; the results are given in Table 2.9b. The consequences of the calculation are now quite satisfactory: The calculated dissolved concentrations are uniformly 0.625 ppb, and the sorbed concentrations reflect the differences in organic carbon content of the system sediments. Note, however, that this computation is valid within the context of the EXAMS program only because sediment transport is not an explicit state variable in the program, i.e., the SEDFL matrix is not a description of sediment transport per se, but merely a computational device for computing the exchange of synthetic organic chemicals across the benthic boundary layer. "Solids balances" and stable bed thicknesses are the responsibility of the user when assembling an environmental description to drive the program; EXAMS simply processes this data (via the SEDFL matrix) to arrive at a proper characterization of chemical transport in the system.

Table 2.9b. EXAMS test of modified dispersive exchange equations

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Unreactive neutral compound -- Koc = 3.E5
ECOSYSTEM: Noname Slough -- Dispersion equation test data
------------------------------------------------------------------------
TABLE 13. DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
------------------------------------------------------------------------
COMP STEADY-STATE RESIDENT MASS    **** TOXICANT CONCENTRATIONS ****
        2                         TOTAL   DISSOLVED SEDIMENTS   BIOTA
     G/M      KILOS         %      MG/*     MG/L      MG/KG      UG/G
--- ------    ------     ------  --------- --------- --------- ---------
  7 2.000E-03 2.0000E-03 100.00  1.000E-03 6.250E-04  3.75
 SUBTOTAL:    2.0000E-03   0.49
 AND IN THE BOTTOM SEDIMENTS:
  8 0.313     0.3125      76.61  9.38      6.250E-04  9.38
  9 9.543E-02 9.5428E-02  23.39  0.188     6.250E-04 0.188
 SUBTOTAL:    0.4079      99.51
TOTAL MASS (KILOGRAMS) =    0.4099
------------------------------------------------------------------------
* TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.
```

A fuller test of EXAMS' transport algorithms can be executed by specifying the ion exchange capacities and organic carbon content of all sediment phases in Noname Slough (Table 2.10), and by coupling the advective transport characteristics (Table 2.6) to a full specification of exchange properties across the benthic boundary layer (Table 2.11). Given a test chemical that is an organic base with, say, a pKb of 7.4, and a KCECG of 250., while retaining the Koc of 3.E5, EXAMS computes the Kp of sediment phases as a function of the pH in each sector of the ecosystem. Given a pH of water column compartments of 8.0, a pH in the Noname Slough muds of 6.0, and a pH of 7.0 in the sand (compartment 9), EXAMS transport profile of the system is given in Table 2.12. Note that the transport profile reflects both physical characteristics of the ecosystem, and interactions of the compound with the chemistry of the system. The residence times in EXAMS' transport profiles, which indicate the local strength of transport processes in each compartment, are thus an amalgam of chemical and physical properties and will, therefore, differ for compounds of differing sorptive properties. In other words, these residence times should not be interpreted in terms of sediment dynamics or hydraulics; they refer to the kinetics of transport of the synthetic organic compounds forming the subject matter of EXAMS.

Table 2.10. Properties of Noname Slough sediments

```
AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Unreactive organic base: Koc = 3.E5, Kcec = 250
ECOSYSTEM: Noname Slough - full transport regime
---------------------------------------------------------------------------
TABLE 5.  INPUT DATA DESCRIBING ENVIRONMENT: SEDIMENT CHARACTERISTICS.
---------------------------------------------------------------------------
  TY    SDCHR       PCTWA        FROC         CEC          AEC        DOC
         (1)         (2)          (3)          (4)          (4)        MG/L
---------------------------------------------------------------------------
  1L    100.0                  2.0000E-02   15.00        12.00
  2B    1.200       180.0      5.0000E-02   10.00        12.00
  3L    100.0                  2.0000E-02   15.00        12.00
  4B    1.200       180.0      5.0000E-02   20.00        14.00
  5L    100.0                  2.0000E-02   15.00        12.00
  6B    1.200       180.0      5.0000E-02   20.00        16.00
  7L    100.0                  2.0000E-02   15.00        12.00
  8B    1.200       180.0      5.0000E-02   25.00        18.00
  9B    1.950       115.0      1.0000E-03  0.1000        0.1000
---------------------------------------------------------------------------
 (1) UNITS: MG/L SUSPENDED SEDIMENT IN L, E, H; BULK DENSITY (G/CC) IN B
 (2) 100 * F.W./D.W. IN B.
 (3) DIMENSIONLESS.
 (4) MEQ/100 GRAMS DRY WEIGHT.
```

Finally, the exposure concentrations resulting from a load of the organic base that contaminates the first sector of Noname Slough to a level of 1 ppb is given in Table 2.13. The dilution effects of bedload transport, groundwater entry (at compartment 6), and the tributary inflow (at compartment 3) can be seen in these results. In this case, the advective flows through the system result in steady-state exposures that differ substantially from a simple chemical equilibrium state. The dispersive exchange terms are nonetheless necessary for a complete description of the system: These terms serve as the only available descriptors of interactions between the bedded sediments of compartments 2, 4, and 6 with their overlying water columns.

Table 2.11. Dispersive transport specifications for Noname Slough

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Unreactive organic base: Koc = 3.E5, Kcec = 250
ECOSYSTEM: Noname Slough - full transport regime
------------------------------------------------------------------------
TABLE 8.  INPUT DATA DESCRIBING ENVIRONMENT: TURBULENT INTERCONNECTIONS.

COMP. NO. (JTURB)        7          8          1          3          5
CONNECTED (ITURB)        8          9          2          4          6
X-SECTION (XSTUR)  1.000E+03  1.000E+03  1.000E+03    800.       200.
CHAR. LN. (CHARL)    1.02       0.175      1.02       1.02       1.02
EDDY DISP. (DSP)   1.500E-04  3.600E-05  1.500E-04  1.500E-04  1.500E-04
```

Table 2.12. Complete transport profile of organic base in Noname Slough

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Unreactive organic base: Koc = 3.E5, Kcec = 250
ECOSYSTEM: Noname Slough - full transport regime
------------------------------------------------------------------------
TABLE 9.  TRANSPORT PROFILE OF ECOSYSTEM.
------------------------------------------------------------------------
CP T*   VOLUME     SEDIMENT  WATER FLOW  SED. FLOW  RESIDENCE TIME (DAYS)
   Y  (CUBIC M)   MASS (KG) (CU. M/DAY) (KG/DAY)     WATER    SEDIMENTS
------------------------------------------------------------------------
  1L  2.000E+03    200.       237.      2.007E+03   8.44     9.966E-02
  2B    50.0     3.333E+04    2.83      3.541E+03   9.41       9.41
  3L  1.600E+03    160.       414.      2.261E+03   3.86     7.077E-02
  4B    40.0     2.667E+04    3.42      4.273E+03   6.24       6.24
  5L   400.        40.0       63.0       561.       6.35     7.128E-02
  6B    10.0     6.667E+03    5.17       468.       1.03      14.2
  7L  2.000E+03    200.       472.      3.216E+03   4.23     6.219E-02
  8B    50.0     3.333E+04    15.1      4.749E+03   1.76      7.02
  9B   300.      5.087E+05    11.3      0.000       6.72
------------------------------------------------------------------------
* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC
```

Table 2.13. Exposure concentrations of organic base in Noname Slough

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Unreactive organic base: Koc = 3.E5, Kcec = 250
ECOSYSTEM: Noname Slough - full transport regime
-----------------------------------------------------------------------------
TABLE 13. DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
-----------------------------------------------------------------------------
COMP STEADY-STATE RESIDENT MASS    **** TOXICANT CONCENTRATIONS ****
       2                             TOTAL   DISSOLVED SEDIMENTS   BIOTA
     G/M        KILOS        %.      MG/*      MG/L      MG/KG      UG/G
--- ------      ------     ------  --------- --------- --------- ---------
  1 2.000E-03 2.0000E-03  62.06  1.000E-03 6.284E-04  3.72
  3 5.039E-04 4.0315E-04  12.51  2.520E-04 1.583E-04 0.936
  5 1.877E-03 3.7547E-04  11.65  9.387E-04 5.898E-04  3.49
  7 4.442E-04 4.4420E-04  13.78  2.221E-04 1.396E-04 0.825
 SUBTOTAL:    3.2228E-03   1.79
 AND IN THE BOTTOM SEDIMENTS:
  2 6.939E-02 6.9387E-02  39.14   2.08      4.155E-04  2.08
  4 3.570E-02 2.8560E-02  16.11   1.07      1.528E-04  1.07
  6 0.138     2.7519E-02  15.52   4.13      5.890E-04  4.13
  8 3.641E-02 3.6411E-02  20.54   1.09      1.364E-04  1.09
  9 1.539E-02 1.5394E-02   8.68  3.026E-02 1.364E-04 3.024E-02
 SUBTOTAL:    0.1773      98.21
TOTAL MASS (KILOGRAMS) =    0.1805
-----------------------------------------------------------------------------
* TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.
```

2.3.1.5 Transport of synthetic organic chemicals

EXAMS uses the transport field defined by WATFL, SEDFL, WATOUL, and SEDOUL to compute first-order coefficients that describe transport of chemical through the ecosystem. These coefficients describe the export of chemicals from the system, and the internal transport of the compound among the compartments used to define different physical sectors of the system.

The WATOUL and SEDOUL vectors are used to compute exports from each compartment. A value of EXAMS' internal vector EXPOKL, with dimensions of (liters/hour), is calculated for each compartment as EXPOKL =

$$\mathrm{ALPHA}(16)*\mathrm{WATOUL} + \mathrm{ALPHA}(17)*\frac{\mathrm{SEDOUL}}{\mathrm{SEDCOL}} + \mathrm{ALPHA}(18)*\mathrm{WATOUL}*\mathrm{PLRAG}$$

where ALPHA(16), (17), and (18) are the total fractions of the chemical in dissolved, sediment-sorbed, and biosorbed states, respectively. The transport of biosorbed material is restricted to the planktonic fraction (user input datum PLRAG). Planktonic organisms are by definition subject to transport by water flows. EXAMS' computations therefore assume that this fraction of the chemical is free to move along all water-transport pathways, rather than imposing a set of special transport rules akin to the sediment transport rules of Section 2.3.1.3.

Pollutants also leave each compartment via water and sediment flow pathways that connect the compartment to other sectors of the ecosystem. From the perspective of the donor compartment, these flows can be represented as a pure export of chemical across the boundaries of the compartment, despite the fact that the material may be returned from the receptor compartment at some later time. Each row of the WATFL and SEDFL matrices gives the flows of water and sediments leaving a compartment, and the row sums are the total local (that is, within-system) outflows from the compartments. For each compartment, EXAMS computes a value of an internal variable (INTOUL, liters/hour) analogous to the export vector EXPOKL. This computation can be represented as INTOUL =

$$\mathrm{ALPHA(16)*SUMWAT + ALPHA(17)*}\frac{\mathrm{SUMSED}}{\mathrm{SEDCOL}}\mathrm{ + ALPHA(18)*SUMWAT*PLRAG}$$

where SUMWAT and SUMSED are the appropriate row sums in the WATFL and SEDFL matrices, and SEDCOL and PLRAG are the sediment:water ratio and planktonic biomass fraction for the donor compartment.

These transport terms (EXPOKL and INTOUL) must now be converted to pseudo-first-order coefficients that express their effect on the concentration of chemical in the source (donor) compartment. This coefficient (CONOUL, dimensions /hour) is computed as:

Eq. 2.79
$$\mathrm{CONOUL} = \frac{\mathrm{EXPOKL + INTOUL}}{\mathrm{WATVOL}}$$

where WATVOL is the volume of water (liters) present in the donor compartment. This coefficient (CONOUL) is the contribution of transport processes to the overall loss constant "K" of Eq. 2.1.

Intra-system transport also imposes chemical loadings on the compartments receiving the contaminated flows (factor "Li" in Eq. 2.1). EXAMS combines the WATFL and SEDFL matrices into a new matrix (INTINL, dimensions liters/hour) needed for computing the internal loadings (Li) on each compartment. Each element of INTINL is first calculated from the sum of corresponding elements in WATFL and SEDFL via the expression:

$$ALPHA(16)*WATFL + ALPHA(17)*\frac{SEDFL}{SEDCOL} + ALPHA(18)*WATFL*PLRAG$$

using values of ALPHA, SEDCOL, and PLRAG for the donor compartment.

Multiplication of each element of INTINL in a given row, by the concentration of chemical in the donor compartment given by the successive column indices of the row, yields the magnitude of the loadings passed to the receptor compartment by each of the donors. The sum of these loadings is the internal load (Li, mg/hr) on the receiving compartment. Li must also be divided by the aqueous volume of the receptor ("V" in Eq. 2.1), in order to express the effect of the internal loadings on the concentration of chemicals in the receptor. EXAMS therefore divides each element of INTINL by the volume of the receiving compartment:

$$INTINL \longleftarrow INTINL/WATVOL$$

and retains the resulting matrix of pseudo-first-order (dimensions /hr) coefficients for subsequent use in its steady-state and kinetic simulation equations (Section 2.5).

2.3.2 Volatilization

EXAMS uses a two-resistance model to compute export of synthetic organics across the air-water interface. The two-resistance or "two-film" models, although originally developed for industrial applications (Whitman 1923), have recently been successfully adapted to environmental problems by Liss (1973), Liss and Slater (1974), Mackay and Leinonen (1975), and Mackay (1978). For its derivation, Whitman (1923) pictured the air-water interface as being composed of "stagnant films" of air and water, bounded by well-mixed bulk phases on either side of the interface (Figure 2.4, redrawn from Liss and Slater 1974). The flux of compound (F, moles/m2/hour) through the aqueous film can be described using Fick's first law:

Eq. 2.80 $$F = D(dC/dZ)$$

where D is the aqueous diffusion constant of the chemical in the film (m2/hr), C is the concentration of unionized, unsorbed compound (mol/cubic m), and dC/dZ is the concentration gradient in the film. The flux of chemical through the stagnant atmospheric layer is, similarly, given by:

Eq. 2.81 $$F = D/RT\ (dP/dZ)$$

where D is now the diffusion constant of the compound in the air layer, dP/dZ is the partial pressure (atmospheres) gradient in

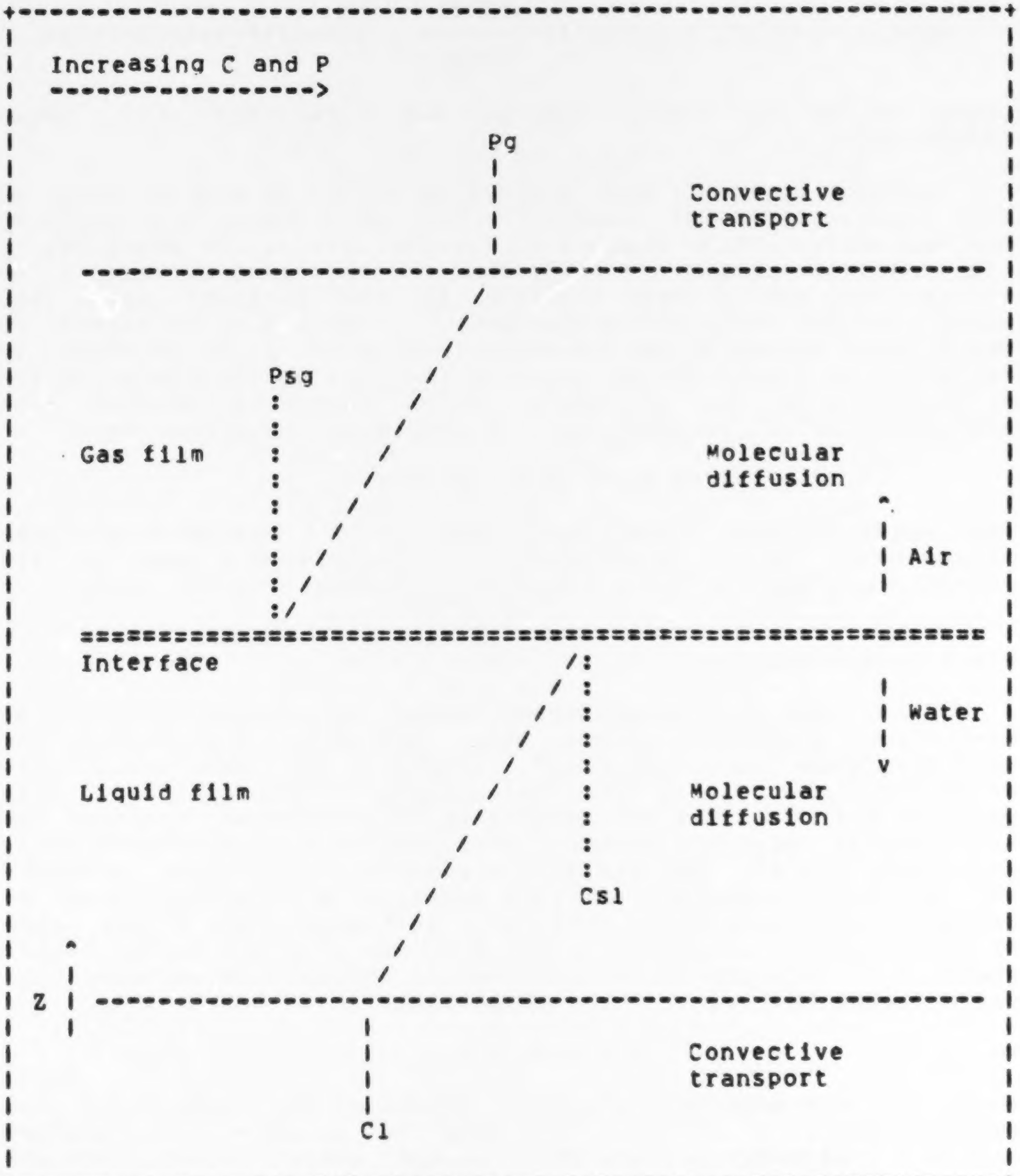
Increasing C and P
Pg
Convective transport
Psg
Gas film
Molecular diffusion
Air
Interface
Water
Liquid film
Molecular diffusion
Csl
Z
Convective transport
Cl

Figure 2.4. Whitman (1923) two-resistance or two-film model of a gas-liquid interface. Cl is concentration (mol/cubic m) in bulk water, Pg is partial pressure (atm) in bulk air, Csl is aqueous concentration in liquid at the interface, Psg is partial pressure on atmospheric side of interface (after Liss and Slater 1974).

the film, R is the gas constant (8.206E-5 cubic m - atm/ mol K), and T is Kelvin temperature.

Environmental gas exchange processes are often formulated in terms of an "exchange constant" k, which expresses the conductivity of the film to gas transport. The exchange constant has dimensions of velocity (m/hr); it is also known as the "mass transfer coefficient," "permeability coefficient," "adsorption/exit coefficient," and "piston velocity." The flux of gas through the stagnant layers is given as

Eq. 2.82 $F = (kl)\, dC$ (liquid phase), or $(kg)\, dP/RT$ (gas phase)

where dC (dP) is the concentration (partial pressure) difference across the film, and $k = D/z$, z the film thicknesses. The reciprocals ($r = 1/k$) of the exchange constants give the transport resistances of the aqueous and atmospheric interface zones.

Given a steady-state transport of gas through the interface, the flux through the stagnant layers of air and water (Figure 2.4) must be the same. Therefore, Eq. 2.82 implies that

Eq. 2.84 $$F = kl\,(Csl - Cl) = kg/RT\,(Pg - Psg)$$

where kl is the liquid phase, and kg the gas phase, exchange coefficient. The partitioning of the exchanging (unionized) substance across the air-water interface is given by Henry's Law:

Eq. 2.85 $$Psg = H\,(Csl)$$

where H is the Henry's Law constant (atm - cu. m/mol). Csl and Psg can be eliminated between Eqs. 2.84 and 2.85, yielding an equation relating the transport flux to the bulk phase concentrations only:

Eq. 2.86 $$F = Kl\,(Pg/H - Cl)$$, where

Eq. 2.87 $$1/Kl = 1/kl + RT/(H*kg)$$

The total resistance to transfer of a gas across the air-water interface ($Rl = 1/Kl$) is thus the sum of the series resistances in the liquid ($1/kl$) and gas ($RT/(H*kg)$) phases of the interface. The two-resistance model assumes that transport resistance at the interface can be neglected; although generally this is the case, under very turbulent conditions or in the presence of surface-active contaminants this assumption is less tenable (Bird, Stewart, and Lightfoot 1960:652).

The "two-film" picture of the air-water interface (Figure 2.4) is physically unrealistic, although events at molecular scales undoubtedly have an effect on interphase transport. Both atmospheric and hydrodynamic eddy turbulence must often extend to the air-water interface, however, and the notion of a discontinuous transition from turbulent flow to a stagnant film near the air-water interface cannot be seriously entertained. The supposition that the interface is composed of stable, uniform films is still less plausible. The two-resistance models do, however, explicitly recognize that transport resistance occurs both in the aqueous and in the atmospheric regions of the air-water interface. There is ample precedent (see, for example, Fischer et al. 1979) for amalgamating the effects of intermittent turbulent and advective transport events occurring in the interfacial zone, into an effective dispersion coefficient D or exchange constant k. Furthermore, predictions derived from two-resistance models usually differ very little from the predictions of more complex (e.g., surface-renewal theory) models (Danckwerts 1970). Laboratory studies of the volatilization of chlorohydrocarbons from dilute aqueous solution Dilling 1977; Dilling, Tefertiller, and Kallos 1975) have provided further evidence that two-resistance models are good predictors of fluxes of organic chemicals across the air-water interface.

A two-resistance model has been used to compute the transport of atmospheric contaminants (sulfur dioxide, carbon tetrachloride, etc.) into the world ocean (Liss and Slater 1974). Such an application requires a knowledge of Pg, the bulk atmospheric partial pressure. Lacking a measured value of Pg, it can in some circumstances (global models, plume (stack gases) dispersion models) be calculated and coupled to a two-resistance interphase transport model. Usually, however, bulk atmospheric transport of organic pollutants volatilized from aquatic systems is so rapid that Pg can be neglected (Mackay and Leinonen 1975, Mackay 1978). This approach was adopted for EXAMS, resulting in a simplification of Eq. 2.86, yielding

Eq. 2.88 $$F = -Kl\ (Cl)$$

Because EXAMS was designed, among other things, for pre-manufacture evaluation of new chemicals, there was, in any case, little likelihood that measured values of Pg would be readily available for use in the model. EXAMS does not entirely preclude atmospheric inputs, however. EXAMS' loading functions allow for entry of spray drift (DRFLDG), and for rain-out (PCPLDG) loadings, where these can be computed (see Section 2.4 for a discussion of pollutant loadings in EXAMS).

For use in EXAMS, Eq. 2.88 must be rephrased to give the effect of volatilization on the concentration of pollutant in each sector of the ecosystem (compartment) having an air-water interface. EXAMS' concentration variable ([C], Eq. 2.1) is the total concentration of pollutant in units of mg/liter of aqueous volume. Multiplication of both sides of Eq. 2.88 by MWTG*AREAG/VOLG, where MWTG is the gram molecular weight of the compound, AREAG is the area of the air-water interface (square meters), and VOLG is the volume (cubic meters) of the compartment, gives

Eq. 2.89 $$d[C]/dt = -(K1*AREAG/VOLG) * (ALPHA(1)) * [C]$$

The additional factor ALPHA(1) is the fraction of the total pollutant concentration [C] present as a volatilizable (unionized, unsorbed) chemical species (Section 2.2.4). The group (K1*AREAG/VOLG)*(ALPHA(1)) is a pseudo-first-order rate constant with units /hr. This rate constant is computed in EXAMS' subroutine "VOLAT;" it is the volatilization contribution to the total pseudo-first-order rate constant given as parameter "K" in Eq. 2.1.

EXAMS' two-resistance model reduces at this point to a computation of the transport resistances (or exchange constants) of chemical pollutants in the liquid (1/kl) and atmospheric (RT/(H*kg)) zones of the air-water interface. These transport resistances are governed by the intensity and duration of physical turbulence and convective motions in the interface zones. Following a suggestion of Liss and Slater (1974), EXAMS indexes the transport resistance of chemical pollutants against the exchange properties of well-studied environmental substances. The transport of oxygen across the air-water interface of aquatic systems (reaeration) has been studied for many years. Oxygen transport is controlled by resistance in the liquid phase (Liss 1973). The exchange constant for dissolved oxygen thus provides a measure of turbulence on the liquid side of the air-water interface. Water itself, as the solvent for chemical pollutants in aquatic systems, has no transport resistance in the liquid phase of the interface: its transport is controlled by events in the atmospheric zone of the interface.

Given exchange constants for oxygen and for water vapor (note that the latter is not the same as the evaporation rate), it remains to index the transport resistances of the pollutant to those of the environmental referents. Several indexing methods have been proposed. Kinetic theory suggests that the average molecular kinetic energies of all chemicals present in a given zone of the interface are the same, and, therefore, that average molecular velocities in a multi-component mixture should distribute in proportion to the square root of the molecular weights of the components. Liss and Slater (1974) suggested this form of indexing. EXAMS uses this method for relating the exchange constant for water vapor to the vapor-phase volatilization resistance of pollutants. The temperature of the vapor is assumed to be the same as the water temperature specified for the appropriate aquatic compartment. EXAMS thus computes the vapor-phase transport resistance (RESGAS) from the equation:

Eq. 2.90 RESGAS = (TKEL*8.206E-5)/(WAT*HENRY*SQRT[18./MWTG])

where TKEL is Kelvin temperature, WAT is the water vapor exchange constant, HENRY the Henry's Law constant, and the molecular weight of water is taken as 18.

Reasoning from the Stokes-Einstein equation, Tsivoglou (1967) suggested that the (liquid-phase dominated) exchange constants for molecular oxygen vs. the normal atmospheric gases (Kr, Ra, He, etc.) are linearly related to their relative molecular diameters or, equivalently, their molecular diffusion constants in water. A literal interpretation of the Whitman "two-film" derivation gives much the same result. Models based on surface-renewal theories suggest, however, that relative exchange constants should vary as the square root of diffusivities (Danckwerts 1970:100). Dobbins (1964) constructed an elegant hybrid of film and surface-renewal theory that collapses to a Whitman model under quiescent conditions, and to a surface-renewal model under more turbulent conditions. He also found, via laboratory studies, that the appropriate root of the diffusivity ratio for the nitrogen/helium gas pair tended from 0.985 to 0.648 with increasing water turbulence, as expected from his theoretical equations. Given the uncertainties in estimating or averaging oxygen exchange constants, however, a full development of the Dobbins model for inclusion in EXAMS seemed unwarranted.

The molecular diffusivity of a new organic chemical is not often known, although it frequently can be estimated from other chemical properties (Reid, Prausnitz, and Sherwood 1977). The molecular weight of an organic compound is almost always available, however, so EXAMS uses Liss and Slater's (1974) molecular weight corrector as its default technique for relating the liquid-phase transport resistance of a pollutant to exchange constants of dissolved oxygen (parameter KO2G). The liquid-phase transport resistance (RESLIQ) is then simply:

Eq. 2.91 RESLIQ = 1./(KO2 * SQRT[32./MWTG])

where KO2 is the oxygen (molecular weight 32) exchange constant. EXAMS, however, also provides a user-specified input parameter (KVOG) that overrides the default procedure when it is non-zero. A user can thereby specify the oxygen exchange index as a simple ratio of diffusivities, a diffusivity ratio to any fractional power, or via an experimental value meausured by the technique of Hill et al. (1976), corrected as appropriate for differences between laboratory and field turbulence conditions. When KVOG is non-zero, EXAMS computes the liquid-phase transport resistance as:

Eq. 2.92 RESLIQ = 1./(KO2*KVOG)

The total transport resistance of the pollutant is the simple sum of the individual phase transport resistances. The exchange constant of the pollutant (EXAMS' parameter "COND" (conductivity)) is the reciprocal of that sum (Kl = COND = 1./(RESLIQ + RESGAS)). EXAMS computes the pseudo-first-order volatilization rate constant as:

$$\mathrm{COND} * \mathrm{ALPHA}(1) * \mathrm{AREAG} / \mathrm{VOLG}$$

as the final computational step in subroutine VOLAT.

2.3.2.1 Chemical data entry

The chemical parameters governing volatilization of a pollutant from aquatic systems can be entered into EXAMS' chemical data base in several ways. The gram molecular weight of the pollutant (MWTG) is required, for computation of the vapor-phase transport index (Eq. 2.90). The Henry's Law constant (HENRY) can be loaded, however, either as a single value of HENRYG (atm-m3/mol), or as a funtion of temperature. When parameter EHENG is loaded as a non-zero value, EXAMS computes the Henry's Law constant at local temperatures TCELG from the relationship:

Eq. 2.93 $$\log(\mathrm{HENRY}) = \mathrm{HENRYG} - \{[1000*\mathrm{EHENG}]/[4.58(\mathrm{TCELG}+273.15)]\}$$

Given a zero value for HENRYG, but a non-zero value for the vapor pressure of the compound, EXAMS internally computes the Henry's Law constant from the vapor pressure/solubility ratio (Mackay and Wolkoff 1973, Mackay and Leinonen 1975). If either the vapor pressure or the solubility of the compound have been entered as functions of temperature, these data are adjusted to local (TCELG) temperatures (via Eq. 2.94 and/or Eq. 2.95), prior to computation of HENRY.

Eq. 2.94 $$\log(\mathrm{VAPR}) = \mathrm{VAPRG} - \{[1000*\mathrm{EVPRG}] / [4.58(\mathrm{TCELG}+273.15)]\}$$

Eq. 2.95 $$\mathrm{SOL} = 1000*\mathrm{MWTG}*\{10**[\mathrm{SOLG} - \{(1000*\mathrm{ESOLG})/[4.58(\mathrm{TCELG}+273.15)]\}\ ]\}$$

Note that, although a simple (temperature invariant) pollutant solubility is entered in units of mg/L (ppm), EXAMS expects solubility as a function of temperature to be entered via the ideal solubility law, that is, as the dependence of molar solubility on temperature.

2.3.2.2 Exchange constants for water vapor

The water vapor exchange constant (WAT, Eq. 2.90) used to compute the vapor-phase transport resistance of pollutants is not itself a direct user input to EXAMS. Liss (1973), in a series of wind-tunnel experiments, found the piston velocity of water vapor to be a linear function of windspeed. EXAMS takes, as its user input variable, the average windspeed at a height of 10 cm above the water surface (input variable WINDG, m/s). The exchange constant for water vapor (WAT) is computed separately for each compartment from these data. Liss' results can be represented via a linear regression equation that includes the shift in units from m/s for wind speed to m/hour for the water vapor exchange constant:

Eq. 2.96 $$WAT = 0.1857 + 11.36 * WINDG$$

in which changes in wind velocity at 10 cm above the water surface (WINDG) account for 98.3% of the variance in the exchange constant for water vapor (WAT, m/hr) over a range of windspeeds from 1.6 to 8.2 m/s.

Windspeeds observed at other heights can be converted to windspeed at 10 cm via the usual assumption of a logarithmic wind profile (Israelsen and Hansen 1962). The numerical result of the conversion depends to some extent on the unit of measurement used for height. More exactly, windspeeds U1 and U2 at heights Z1 and Z2 are related by:

$$U1/U2 = \log(Z1/Zo)/\log(Z2/Zo)$$

where Zo is the "effective roughness height." The roughness height is generally on the order of one millimeter; wind measurement heights thus should be expressed in mm in order to achieve a vertical translation of an observed windspeed datum. For example, many terrestrial USA weather stations measure windspeeds at 18-20 feet (6 m) above ground level. Windspeed at 10 cm can be estimated by multiplication of this datum by (log 100)/(log 6000), that is, by reducing the observation by a factor of 1.89. The standard observational height for windspeed data in oceanographic investigations is 10 m, in this case requiring reduction of the data by a factor of 2, to generate values of WINDG for EXAMS.

2.3.2.3 Exchange constants for molecular oxygen

Hydrodynamic turbulence near the air-water interface is generated by a variety of mechanisms. In swiftly flowing streams and rivers, bed shear stress on the moving waters generates eddy turbulence that can keep the entire water column in a state of constant agitation. Where rivers widen into coastal estuaries, advection velocities decrease, but the motion of the tides tends to maintain strong turbulence in the surface waters. In lakes and in the open ocean, wind stress is a primary force producing turbulent motions in the upper part of the water column. Wind waves travel far beyond the storm systems producing them in the largest lakes and in the oceans, and the great ocean currents and upwelling zones generate upper water turbulence beyond that attributable to the winds alone. In smaller lakes, wind stress may be directly responsible for most of the hydrodynamic motion in the system.

EXAMS requires an oxygen exchange constant as an input datum for each compartment from which a pollutant can volatilize. The input datum (KO2G, cm/hr) is assumed to be the exchange constant measured at 20 degrees C, or corrected to that temperature. EXAMS uses the conventional engineering correction (equivalent to an Arrhenius expression) for converting KO2G to the temperature (TCELG) of each compartment (Kramer 1974):

Eq. 2.97 KO2L = (KO2G/100.) * (1.024)**(TCELG - 20.)

(KO2G is also divided by 100 to convert cm/hr to m/hr).

Reaeration rates can be measured in the field in a number of ways, including tracer techniques (Tsivoglou, McClanahan, and Sanders 1972) and oxygen release into a nitrogen-sparged dome (Copeland and Duffer 1964, Hall 1970). Lacking measured values, oxygen exchange constants can in many instances be estimated from other properties of the system. Kramer (1974) has briefly reviewed the available predictive equations for estimating oxygen exchange coefficients in streams and rivers. Most of these contain terms for flow velocities and depth. Many also include longitidunal dispersion coefficients, energy grade lines, and channel widths. Although predictive equations have been successfully used for riverine systems, generally these equations significantly under-predict reaeration in estuarine systems. Oxygen exchange constants in rivers are generally on the order of 5 to 20 cm/hr. In estuaries, exchange constants of 4 to 25 cm/hr, and as large as 100 cm/hr, have been observed. Liss and Slater (1974) estimated an average exchange constant for the open sea of 20 cm/hr.

In lakes and ponds, reaeration may be primarily determined by the local winds. Banks (1975, Banks and Herrera 1977) showed that the effect of wind on reaeration rates can be separated into two distinct zones. At windspeeds (at 10 m height) less than about 5.5 m/s, exchange constants correlate with the square root of windspeed. At higher windspeeds, the exchange constant increases as the square of the wind velocity. Banks (1975) gives:

Eq. 2.98 KL = (4.19E-6) SQRT(U) for U < 5.5 m/s

Eq. 2.99 KL = (3.2E-7) U**2 for U > 5.5 m/s

where KL is the oxygen exchange constant (in m/s) and U is windspeed (m/s) at 10 m above the water surface. Over a range of windspeeds from 1 to 30 m/s, the oxygen exchange constant thus would change from 1.5 to 104 cm/hr.

2.3.2.4 Example applications

A number of reports on volatilization from natural water bodies have been published. These studies provide good illustrations of of the general utility and level of reliability of the two-resistance model used for EXAMS.

2.3.2.4.1 Radon in small lakes in the Canadian Shield

Emerson (1975) conducted an experimental investigation of the loss of radon gas (Rn 222) from small lakes in Canada's Experimental Lakes Area (ELA). He reported his results in terms of exchange constants for Rn gas; the "best estimate" was 0.16 to 0.40 m/day. Average wind velocities, measured 1 m above the water surface, were about 1.5 m/s. Summer epilimnion temperatures in these lakes are about 20 degrees C (Schindler 1971). Windspeed and temperature suffice, given the Henry's Law constant for Rn, to derive an independent estimate of the Rn exchange constant from EXAMS' two-resistance model.

EXAMS computes both a gas- and liquid-phase transport resistance. Rn transport is usually controlled by the liquid-phase resistance. Under a sufficiently stagnant airmass, however, gas-phase resistance can be greatly magnified. In this instance, computation of the gas-phase resistance serves to illustrate EXAMS' procedure, and to demonstrate that Rn transport is controlled by events in the liquid phase of the air-water interface of these lakes.

Wilhelm, Battino, and Wilcock (1977) give the aqueous solubility of radon gas as the mole fraction under 1 atm partial pressure. The Henry's Law constant (atm-m3/mol) of Rn gas between 0 and 50 degrees C can be computed from their data:

T(deg. C):	0	5	10	15	20	25	30	35	40	45	50
mol frXE4:	4.24	3.40	2.77	2.31	1.95	1.68	1.46	1.29	1.16	1.05	0.96
HENRYX100:	4.25	5.31	6.50	7.81	9.24	10.8	12.3	14.0	15.6	17.2	18.8

Regression of these data on the model

$$HENRY = A \exp(-B/RT)$$

where R is the gas constant (1.9872 cal/deg mol) and T is Kelvin temperature, yields A = 660.5 and B/R = 2615, accounting for 99% of the variation in HENRY with temperature. EXAMS' input data thus could include:

$$\text{HENRYG} = \log A = 2.82$$

and

$$\text{EHENG} = (B/R) * R * 0.001\ (\text{kcal/cal}) = 5.197\ \text{kcal/mol}$$

EXAMS would then compute local (compartment-specific) values of the Henry's Law constant for Radon, as a function of environmental temperatures (TCELG), via Eq. 2.93. In what follows, the Henry's Law constant at 20 degrees C will be taken as 0.09239 atm-m3/mol.

A piston velocity for water vapor (WAT, Eq. 2.96) can be computed from the observed windspeed datum (1.5 m/s at 1000 mm height). EXAMS' input datum (WINDG) is referenced to a 10 cm height above the water surface. The observed windspeed can be corrected to a 10 cm height by assuming a logarithmic wind velocity profile:

$$\text{WINDG} = 1.5\ (\log 100 / \log 1000) = 1.0\ \text{m/s}$$

The water vapor exchange constant (Eq.2.96) is then:

$$\text{WAT} = 0.1857 + (11.36)(1.0) = 11.5\ \text{m/hr}$$

and the gas-phase transport resistance (RESGAS, here Rg, Eq. 2.90) is:

$$\text{Rg} = (293.15*8.206\text{E-}5) / (11.5*0.09239*\text{SQRT}[18/222]) = 0.079\ \text{hr/m}$$

Emerson's (1975) investigations were conducted in small (3.6-5.6 ha), shallow (mean depth 3.6-5.6 m) dimictic lakes with relatively long hydraulic residence times (3.2-4.2 yr) (Brunskill and Schindler 1971). The hydrodynamics of these lakes are clearly dominated by wind stress, and Banks' (1975) equations (Eqs. 2.98 and 2.99) can be used to estimate an exchange constant for molecular oxygen. The input datum for these equations should be referenced to a height of 10 m above the water surface. The observed datum thus must be translated to 10-m height via:

$$U = 1.5\ (\log 10000 / \log 1000) = 2.0\ \text{m/s}$$

U is less than 5.5 m/s; Eq. 2.98 therefore applies and KL = 4.19E-6 SQRT(2.0) = 5.93E-6 m/s. EXAMS' input datum (KO2G) has dimensions of cm/hr; the units conversion yields KO2G = 2.13 cm/hr.

EXAMS' default technique for estimating the liquid-phase transport resistance uses the molecular weight of the pollutant as an indexing factor. The temperature of the epilimnion (20 degrees C) in this case obviates the need for conversion of KO2G to a differing value at the temperature of the environment (Eq. 2.97). The liquid-phase Rn transport resistance (RESLIQ in Eq. 2.91, here designated Rl) can be computed as:

Rl = 1/(0.0213 * SQRT[32/222]) = 123.66 hr/m

Resistance in the liquid phase thus amounts to 99.9% of the total Rn transport resistance (Rt = Rg + Rl = 123.74 hr/m). The estimated exhange constant for Rn gas is therefore 1/Rt = 8.08E-3 m/hr = 0.19 m/day, which value can be compared to Emerson's (1975) experimental estimate of 0.16 - 0.40 m/day.

EXAMS also allows for the entry of a user-specified liquid-phase transport index (KVOG, Eq. 2.92), where this parameter has been measured experimentally, or has been estimated from the aqueous diffusivity of the pollutant. Emerson (1975, citing Rona (1918) via Peng (1973)) gives a diffusion constant for Rn of 1.37E-5 cm2/s at 25 degrees C. The diffusion constant of molecular oxygen in water at 25 degrees is 2.41E-5 cm2/s (Vivian and King 1964, cited from Reid, Prausnitz, and Sherwood 1977:576). The diffusivity ratio (KVOG = D(Rn)/D(O2)) is thus 1.37/2.41 = 0.568. Application of Eq. 2.92 then yields a liquid-phase transport resistance in these small lakes of:

Rl = 1/[(0.0213)(0.568)] = 82.6 hr/m

and a Rn exchange constant (1/(Rl+Rg)) of 0.29 m/day. Tsivoglou (1967) measured simultaneous exchange constants for oxygen and Rn in laboratory experiments, arriving at a value of KVOG = 0.70. (This value corresponds to the 0.63 root of the diffusivity ratio.) Application of Eq. 2.92 in this case yields Rl = 1/(.0213)(0.70) = 67.1 hr/m, and a Rn exchange constant of 0.36 m/day.

EXAMS' estimates of the Rn exchange constant (0.19, 0.29, and 0.36 m/day) thus encompass essentially the same range as Emerson's (1975) experimental "best estimates" of 0.16 to 0.40 m/day. The critical element in an accurate application of EXAMS to this situation is obviously, therefore, the selection of appropriate values for the environmental driving variables (WINDG and KO2G), rather than the choice of a method of indexing Rn transport against EXAMS' environmental descriptors. Liss and Slater (1974) have estimated average exchange constants for oxygen (20 cm/hr) and water vapor (3000 cm/hr) applicable to the surface of the open sea. These values have on occasion been used to estimate the volatilization of pollutants from inland waters. For Rn transport in these small ELA lakes, use of Liss and Slater's (1974) oceanic exchange constants would give:

$$Rg = (293.15*8.206E-5)/(30.0*0.09239*SQRT[18/222]) = 0.0305 \text{ hr/m}$$

$$Rl = 1/(0.2*SQRT[32/222]) = 13.17 \text{ hr/m}$$

$$Rt = Rg + Rl = 13.2 \text{ hr/m}$$

and a Rn exchange constant (1/Rt) of 1.8 m/day. The fallacy of an uncritical extrapolation of environmental driving forces (in this case the reaeration rate) between systems is apparent: The ELA Rn exchange constant, estimated from oxygen and water vapor transport in the open sea, is an order of magnitude too large, as compared with either the measured values, or to estimates from EXAMS' two-resistance models parameterized via windspeed and Banks' (1975) compilation of reaeration rates as a function of wind velocity.

2.3.2.4.2 1,4-dichlorobenzene in Lake Zurich

Schwarzenbach and coworkers (1979) conducted a one-year study of the fate and transport of 1,4-dichlorobenzene (DCB) in Lake Zurich, Switzerland. Contaminated effluents from waste-water treatment plants are the primary source of DCB loadings entering the lake. The concentration of DCB in these effluents is relatively constant among treatment plants and over time, providing an opportunity for a case-history trial of EXAMS' steady-state evaluative capabilities.

DCB is not subject to appreciable degradation by chemical or biochemical processes in aquatic systems (Callahan et al. 1979); its behavior is governed by volatilization, transport, and sorption phenomena. EXAMS in this instance requires 4 chemical descriptors: the molecular weight (MWTG), solubility (SOLG), octanol-water partition coefficient (KOWG), and Henry's Law constant (HENRYG). The molecular weight of DCB ($C_6H_4Cl_2$) is 147.0. The aqueous solubility and octanol-water partition coefficient of DCB have been measured by Banerjee and coworkers (1980). DCB is soluble to 0.502 mM in water at 25 degrees C (SOLG = 73.8 ppm). Its octanol-water partition coefficient (KOWG) is 2340.

The Henry's Law constant of DCB has not been measured, but it can be estimated (for 25 degrees C, the temperature of the solubility observation) from the vapor pressure/solubility ratio (Mackay and Wolkoff 1973, Mackay and Leinonen 1975). Para-DCB is a solid at normal environmental temperatures (mp 53.1 degrees C (Weast 1971)). The vapor pressure (Pv) of solid 1,4-DCB at 10, 30, and 50 degrees C is 0.232, 1.63, and 8.435 torr, respectively (Darkis, Vermillion, and Gross 1940). Regression of these data on the model $Pv = A \exp(-B/T)$ yields A = 9.63E11, B = 8223, and accounts for 99.99% of the variation in Pv with temperature. EXAMS could be loaded with the results of this regression analysis, i.e., VAPRG = log A = 11.98, and EVPRG = (B)(R)(0.001) = 16.34 kcal/mole. Alternatively, the Henry's Law constant can be estimated via interpolation of the observed vapor pressure to 25 degrees C. The latter procedure was used for this analysis of DCB in Lake Zurich. The interpolated value of Pv is 1.011 torr at 25 degrees C. The Henry's Law constant is therefore (1.011/760)/0.502 = 2.66E-3 atm-m3/mol.

EXAMS also requires environmental input data describing Lake Zurich. In this case, a "canonical" data set need only include information relevant to transport, sorption, and volatilization of neutral organics. Schwarzenbach and coworkers (1979) restricted their investigation to the central basin of Lake Zurich. Both the upper and the central basins receive DCB-contaminated waste-water effluents. The central basin can be modeled in isolation, however, by treating inputs from the upper basin as advected loadings to the (downstream) central basin. Except as noted otherwise, the environmental description given below was drawn from Schwarzenbach et al. 1979.

The central basin has an average hydraulic residence time of 1.2 yr. Banks' (1975) method for estimating KO2G from windspeed thus seems most appropriate, lacking extensive direct field measurements of the oxygen exchange constant. The annual mean windspeed for the period 1955-63, 65-69 was 2.6 m/s (5.1 kt) (unpublished data for Zurich, Switzerland/ Kloten, summarized by USAF ETAC, supplied courtesy of NOAA). Although a station history was not available, these data were in all probability collected at the conventional meteorological screen height (6 m). Windspeed at 10 m height would be 2.6(log 10000/log 6000) = 2.75 m/s. Computation of KO2G via Eq. 2.98 then gives:

KO2G = (4.19E-6) (SQRT[2.75]) (3600 s/hr) (100 cm/m) = 2.5 cm/hr

Average windspeed at 10 cm height (EXAMS' input parameter WINDG) would be 2.6(log 100/log 6000) = 1.38 m/s.

The mean depth of the central basin is 50 m, and the surface area is 68 km2, giving a total volume of 3.4E9 m3. The lake stratifies during the summer (May through September); the thermocline sets up at a depth of 10 m by early May and remains at about that depth until fall turnover (Li 1973). A simple "box" model of the lake can be constructed for EXAMS by dividing the lake into 3 vertical zones, each with an area (AREAG) of 68 km2 or 6.8E7 m2. For the epilimnion segment (compartment 1, TYPE(1) = "E"), DEPTHG(1) = 10 (m), and VOLG(1) = 6.8E8 (m3). The hypolimnion (2, TYPE(2) = "H") then has DEPTHG(2) = 40, and VOLG(2) = 6.8E7*40 = 2.72E9 m3. Assuming a 2 cm depth of active benthic sediments (3, TYPE(3) = "B") gives DEPTHG(3) = 0.02, and VOLG(3) = 1.36E6 m3.

Li (1973) computed the vertical eddy diffusion coefficient in Lake Zurich, as a function of depth and season, from observed monthly temperature profiles averaged over 10 years of record. The annual mean temperature of the epilimnion (0 - 10 m depth, TCELG(1)) was 11 degrees C; the mean hypolimnion temperature was 5.6 degrees C (TCELG(2)). The eddy dispersion coefficient at 10 m depth averaged 0.058 cm2/s during the stratified period and was about 1 cm2/s during the balance of the year. The annual mean value (DSPG for parameterizing average transport between the epilimnion and hypolimnion) was 0.6 cm2/s; EXAMS' input value of DSPG = 0.2 sq m/hr. The dispersion coefficient for exchange between the hypolimnion and benthic sediments (Section 2.3.1.4) was taken as 1.E-4 m2/hr.

In order to compute sorption of DCB to sediment phases, EXAMS requires a description of the benthic and suspended sediments in the system (FROCG, SDCHRG, PCTWAG). Given the size of Lake Zurich (i.e., the relatively small overall sediment:water ratio), and the small octanol:water partition coefficient of DCB (2340), DCB will occur primarily in the dissolved state in the water column of this lake. The values chosen for FROCG, SDCHRG, and PCTWAG are therefore not critical to the outcome of the simulation, so long as they are representative. Table 2.14 summarizes the observed and assumed values that were used to describe the central basin of Lake Zurich to EXAMS.

Table 2.14. Environmental data for central basin of Lake Zurich

Parameter	Compartment		
	1	2	3
TYPE	E	H	B
AREAG, m2	6.8E7	6.8E7	6.8E7
DEPTHG, m	10	40	0.02
VOLG, m3	6.8E8	2.72E9	1.36E6
SDCHRG	5 (mg/L)	5 (mg/L)	1.5 (g/cc)
PCTWAG			150.
FROCG	0.02	0.02	0.02
KO2G, cm/hr@20 C	2.5		
WINDG, m/s@10 cm	1.38		

The combined flow from the upper basin (2500), small creeks draining into the central basin (100), and treatment plant effluents (28) was 2628.E6 cubic m/yr, giving STFLOG(1) = 3.E5 m3/hr. The total load of DCB on the central basin was 88 kg/yr, of which 25 kg derived from the upper basin, 62 kg from treatment plant effluents discharged into the central basin, and 1 kg/yr from other minor sources. For the EXAMS simulation, these loadings were summed to give a STRLDG(1) to the epilimnion of the central basin of 0.010 kg/hr. (Section 3.3.4 demonstrates the entry of this data into EXAMS, and the command sequences used to conduct the analysis.)

EXAMS' resulting output tables (Tables 2.15 and 2.16) predict a flux of DCB to the atmosphere of 59.4 kg/yr, water-borne exports of 28.2 kg/yr, and a total mass of 36.5 kg DCB resident in the water column (DCB concentration 10.7 ng/L). By comparison, Schwarzenbach et al. (1979) estimated a resident mass of 38 kg (11.2 ng/L) in the lake, and, from a mass balance for DCB, estimated the flux to the atmosphere to be 60 kg/yr, with a water-borne export of 28 kg/yr.

Table 2.15. Predicted concentration and resident mass of DCB

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DICHLOROBENZENE
ECOSYSTEM: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
-----------------------------------------------------------------------
TABLE 13. DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
-----------------------------------------------------------------------
COMP STEADY-STATE RESIDENT MASS      **** TOXICANT CONCENTRATIONS ****
       2                              TOTAL   DISSOLVED SEDIMENTS   BIOTA
    G/M        KILOS         %         MG/*      MG/L      MG/KG     UG/G
--- ------    ------      ------   --------- --------- --------- ---------
  1 1.074E-04  7.302       20.00  1.074E-05 1.074E-05 2.060E-04 0.000
  2 4.295E-04  29.21       80.00  1.074E-05 1.074E-05 2.060E-04 0.000
 SUBTOTAL:     36.51       99.22
 AND IN THE BOTTOM SEDIMENTS:
  3 4.228E-06 0.2875      100.00  2.114E-04 1.074E-05 2.060E-04 0.000
 SUBTOTAL:    0.2875        0.78
TOTAL MASS (KILOGRAMS) =      36.80
-----------------------------------------------------------------------
* TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.
```

During the stratified period, contaminated treatment plant effluents spread laterally through the metalimnion of the lake and mix with both the hypolimnion and the epilimnion (Schwarzenbach et al. 1979). Assuming that the summertime loadings mix upward and downward in equal measure, EXAMS' loadings can be modified to account for this phenomenon. The summer (5 month) DCB load to the hypolimnion would amount to (5/12)(62)/2 kg/yr, which can be entered to EXAMS as a "drift" load (DRFLDG(2)) of 1.5E-3 kg/hr. Proportionate reduction of the DCB load on the epilimnion gives STRLDG(1) = 8.5E-3 kg/hr. Given this modification, EXAMS predicted a larger concentration of DCB in the hypolimnion (13.5 ng/L), and a resident mass of 44.0 kg DCB; the predicted fluxes and DCB concentration in the epilimnion (10.7 ng/L) were unchanged.

Table 2.16. Summary of EXAMS' results for DCB in Lake Zurich

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DICHLOROBENZENE
ECOSYSTEM: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
-----------------------------------------------------------------------
TABLE 17.  EXPOSURE ANALYSIS SUMMARY.
-----------------------------------------------------------------------
EXPOSURE:
 A. MAXIMUM CONC. IN WATER COLUMN: 1.07E-05 MG/L DISSOLVED, 1.07E-05 TOT
    MAX. CONC. IN BOTTOM SEDIMENT: 1.07E-05 MG/L DISSOLVED IN PORE WATER
 B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON: 0.00     UG/G
                                       BENTHOS:  0.00     UG/G
 C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS: 2.11E-04 MG/KG (DRY WEIGHT)
FATE:
 A. TOTAL STEADY-STATE ACCUMULATION:  37.     KG; 99.22% IN WATER COL.,
        0.78% IN BOTTOM SEDIMENTS.
 B. TOTAL LOAD: 0.24     KG/DAY - DISPOSITION:   0.00% VIA CHEMICAL
      TRANSFORMATIONS,   0.00% BIOTRANSFORMED,  67.79% VOLATILIZED,
       32.21% EXPORTED VIA OTHER PATHWAYS.
PERSISTENCE:
 A. AT THE END OF A  216.     DAY RECOVERY PERIOD, THE WATER COLUMN HAD
      LOST  50.51% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD
      LOST  19.54% OF THEIR INITIAL BURDEN (  50.26% REMOVAL OVERALL).
 B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY 36. MONTHS.
```

A test of other transport indices requires knowledge of DCB diffusivity. The aqueous diffusivity of DCB can be estimated from molar volume at the normal boiling point (Vb), and Vb can itself be estimated from Vc, molar volume at the critical temperature (Reid, Prausnitz, and Sherwood 1977). Vc for p-DCB is 372 cc/g-mol; Vb = 0.285(Vc**1.048) (Tyn and Calus method) = 140.9 cc/g-mol. The aqueous diffusivity of p-DCB at 25 degrees C, computed via the Hayduk-Laudie revision of the Othmer-Thakar relationship, is (13.26E-5)(0.8904**(-1.4))(140.9**(-.0589)) = 8.46E-6 cm2/s, taking the viscosity of water at 25 degrees C as 0.8904 cp (Weast 1971:F-36). The diffusivity ratio D(DCB)/D(O2), given the diffusivity of molecular oxygen D(O2) as 2.41E-5 cm2/s, is 0.35; its square root is 0.59.

Substituting these values (via KVOG) for EXAMS' default molecular weight transport index (SQRT(32/147) = 0.47) gave estimated resident DCB masses of 43.8 kg (12.9 ng/L), and 31.0 kg (9.1 ng/L), respectively. Simulation using Liss and Slater's

(1974) open-sea transport parameters (with the molecular weight transport index) predicted a resident mass of only 6.6 kg (2.0 ng/L). These comparisons are summarized in Table 2.17. The default molecular weight transport index provided the most accurate prediction of the volatilized flux of DCB from Lake Zurich. As was the case for Rn transport in ELA lakes, however, the selection of proper values for environmental driving forces seems to be more critical, than is the choice taken among methods of indexing pollutant transport across the air-water interface against its environmental referents.

Table 2.17. Results of EXAMS simulations of the behavior of DCB (1,4-dichlorobenzene) in Lake Zurich, Switzerland. Predicted concentration, resident mass in water column, and fluxes vary as a function of load routing, method used to index interphase transport against its environmental referents, and environmental transport parameters.

Method	Concentration, ng/L	Mass, kg	Volatilization, kg/yr	Export, kg/yr
Measured	11.2	38.	60.	27 + 1
SQRT(32/147)	10.7	36.5	59.4	28.2
Partial load to Hypolimnion	10.7(E) 13.5(H)	44.0	59.4	28.2
D(DCB)/D(O2)	12.9	43.8	53.7	33.9
$\text{SQRT}\ \frac{D(DCB)}{D(O2)}$	9.1	31.0	63.7	24.0
SQRT(32/147), KO2=20cm/hr, WAT=30m/hr	1.95	6.64	82.5	5.13

2.3.3 Direct Photolysis

EXAMS includes two entirely separate subroutines that compute rates of direct photolysis. These subroutines are mutually exclusive, and accept different kinds of input data. The first subroutine, PHOTO1, begins from a pseudo-first-order rate constant (KDPG) respresenting the photolytic decomposition rate in near-surface waters under cloudless conditions at a specified latitude (RFLATG). The second subroutine, PHOTO2, works from measured light absorption spectra and reaction quantum yields of the compound. EXAMS selects the appropriate routine via an audit of the structure of the chemical input data. For each existing ionic species (SH2, SH-, S=, SH3+, SH4++; see SPFLG and Section 2.2.1), a positive value of KDPG invokes execution of PHOTO1. When an entry for KDPG is zero, but at least one value of ABSG, the light absorption spectrum of the molecule, is non-zero, EXAMS calls on subroutine PHOTO2 to compute the photolysis rate. (Technically this test is executed on a summation of the ABSG vector of the ionic species; a positive value of this sum (internal variable ABSTOL) and a zero KDPG invoke the call to PHOTO2.) Note that the structure of this decision in effect gives KDPG a higher computational priority than ABSG, that is, if both KDPG and ABSG are positive, EXAMS will use PHOTO1 and KDPG for its computations, and will ignore the absorption spectrum. If PHOTO2 is the preferred computational mechanism, the KDPG vector must contain zero values in the data base.

The techniques used within EXAMS for computing rates of direct photolysis have been derived from the work of Zepp and coworkers (Zepp 1978; 1980; Miller and Zepp 1979a, 1979b; Zepp and Baughman 1978; Zepp and Cline 1977; Zepp et al. 1975, 1976, 1977). Zepp (1980), and Zepp and Baughman (1978) have recently summarized techniques for predicting direct photolysis in natural waters; a computer code for evaluating this transformation pathway has been described by Zepp and Cline (1977).

2.3.3.1 Direct photolysis in aquatic systems

Direct photochemical reactions are a consequence of the absorption of electromagnetic energy by a pollutant molecule. In this "primary" photochemical process, absorption of a photon promotes the molecule from its ground state to an electronically excited state. The excited molecule then either reacts to yield a photoproduct, or decays via some other mechanism (fluorescence, phosphorescence, etc.) back to the ground state. The efficiency of each of these energy conversion processes is called its "quantum yield;" the law of conservation of energy requires that the primary quantum efficiencies sum to 1.0. These ideas are expressed by two fundamental laws of photochemistry. The first, the "Grotthus-Draper" law, states: "Only the light which is absorbed by a molecule can be effective in producing photochemical change in the molecule." Simple irradiation of a system does not necessarily result in photochemical reactions; the light must be of wavelengths that can be absorbed by the chemical. Conversely, laboratory irradiation of a chemical with wavelengths that are not found in natural waters (<290 nm) is of diminished value for predicting the behavior of the compound in the environment. The second law of photochemistry, the "Stark-Einstein" law, was formulated after the discovery that interactions of light and matter are restricted to discrete (quantized) events. This second law in its modern form (Calvert and Pitts 1966:20) states: "The absorption of light by a molecule is a one-quantum process, so that the sum of the primary process quantum yields must be unity."

The rate of photolytic transformations in aquatic systems depends upon both the light intensity in the medium (in other words, the dose rate), and on the response of the irradiated pollutant. The chemical response is composed of two factors: the pollutant's absorption spectrum (EXAMS' variable ABSG), and its quantum efficiency for photochemical transformations (reaction quantum yield, QUANTG). The logic of the situation can be developed in terms of monochromatic light, with spectral effects subsequently incorporated via integration or summation across the solar spectrum. In EXAMS, the solar spectrum is subdivided into 39 wavelength intervals (Table 2.18), and the total rate constant is computed as the sum of contributions from each spectral interval. In what follows, however, the spectral subscripts have in most cases been omitted, in the interest of notational simplicity.

Light intensity decreases exponentially with depth in any absorbing medium. This phenomenon is known as the Beer-Lambert law, and can be stated mathematically as:

Eq. 2.100 $$d(Eo)/dz = -K(Eo)$$

where Eo = photon scalar irradiance, photons/cm2/sec

z = depth, m (DEPTHG)

K = diffuse attenuation coefficient for irradiance, /m, and

Eq. 2.101 $$K = Da + (Bb)$$ (Smith and Tyler 1976),

where D is the mean optical path per unit z (dimensionless), a is the absorption coefficient for the medium (/m), and (Bb) is the back-scattering coefficient. Although seldom measured in freshwater systems, back-scattering is generally very small in marine waters and can be neglected (Jerlov 1976).

Photon scalar irradiance (Eo) is the sum of two contributing light fields in natural waters, the downwelling (Ed) and upwelling (Eu) irradiances. Field measurements, although for the most part restricted to marine systems, have in almost all cases resulted in measured values of Eu of only 2% or less of Ed. Upwelling irradiance can contribute significantly to Eo at

Table 2.18. Spectral intervals used in EXAMS (Zepp and Cline 1977), and spectral absorption coefficients of water (Smith and Baker 1980), chlorophylls + pheophytins (Smith and Baker 1978b), (humic) dissolved organic carbon (unpublished data of R.G. Zepp), and suspended sediments (Miller and Zepp 1979a)

Waveband			Spectral Light Absorption Coefficients			
No.	Center, nm	Width, nm	Water /m (WATETA)	Pigments /m/(mg/L) (PIGETA)	DOC /m/(mg/L) (DOCETA)	Sediments /m/(mg/L) (SEDETA)
1	297.5	2.5	0.160	---	6.30	0.34
2	300.0	"	0.141	---	6.12	"
3	302.5	"	0.133	---	5.94	"
4	305.0	"	0.126	---	5.76	"
5	307.5	"	0.119	---	5.57	"
6	310.0	"	0.105	---	5.39	"
7	312.5	"	0.0994	---	5.22	"
8	315.0	"	0.0952	---	5.06	"
9	317.5	"	0.0903	---	4.90	"
10	320.0	2.5	0.0844	---	4.74	"
11	323.1	3.75	0.0793	---	4.56	"
12	330.0	10.0	0.0678	---	4.17	"
13	340.0	"	0.0561	---	3.64	"
14	350.0	"	0.0463	55.	3.15	"
15	360.0	"	0.0379	55.	2.74	"
16	370.0	"	0.0300	51.	2.34	"
17	380.0	"	0.0220	46.	2.00	"
18	390.0	"	0.0191	42.	1.64	"
19	400.0	"	0.0171	41.	1.39	"
20	410.0	"	0.0162	39.	1.19	"
21	420.0	"	0.0153	38.	1.02	"
22	430.0	"	0.0144	35.	0.870	"
23	440.0	"	0.0145	32.	0.753	"
24	450.0	"	0.0145	31.	0.654	"
25	460.0	"	0.0156	28.	0.573	"
26	470.0	"	0.0156	26.	0.504	"
27	480.0	"	0.0176	24.	0.444	"
28	490.0	10.0	0.0196	22.	0.396	"
29	503.75	17.5	0.0295	19.	0.357	"
30	525.0	25.0	0.0492	14.	0.282	"
31	550.0	"	0.0638	10.	0.228	"
32	575.0	"	0.0940	8.	0.188	"
33	600.0	"	0.244	6.	0.158	"
34	625.0	"	0.314	5.	---	"
35	650.0	"	0.349	8.	---	"
36	675.0	25.0	0.440	13.	---	"
37	706.25	37.5	0.768	3.	---	"
38	750.0	50.0	2.47	2.	---	"
39	800.0	50.0	2.07	0.	---	0.34

visible wavelengths in the clearest ocean waters, however, where molecular back-scattering can be significant, and over white sandy bottoms of high albedo (Jerlov 1976). In the following discussion, photon irradiance is designated "E" and is treated as being identical with Ed or Eo; Eu is assumed to be insignificant.

Integration of Eq. 2.100 yields an expression for the residual irradiance after transmission through a homogeneous layer of depth z:

Eq. 2.102 $$E(z) = E(0)\exp(-Kz) = E(0)\exp(-Daz)$$

where E(0) is the irradiance at the top of the layer. The rate of light absorption in the layer, Ew (photons/cm2/s), is (E(0) - E(z)), or

Eq. 2.103 $$Ew = E(0)\,(1 - \exp(-Kz))$$

For photochemical purposes, it is most convenient to express light absorption on a volumetric molar basis (Bailey et al. 1979:223) (one mole of photons is an Einstein, E). The rate of light absorption Iw, in E/liter/s, is:

Eq. 2.104 $$Iw = \frac{Ew}{(A)(z)} * (1000\ cm3/l) * (0.01\ m/cm)$$

where A = 6.023E23 photons/mole (Avogadro's number). Denoting E(0)/A as Io (E/cm2/s), the volumetric absorption rate Iw is:

Eq. 2.105 $$Iw\ (E/liter/s) = 10\,(Io/z)\,(1 - \exp(-Kz))$$

The electronic absorption spectra of synthetic organic chemicals are usually reported as (decadic) molar absorptivites or extinction coefficients, with units /cm/(mole/liter) or /cm/M (EXAMS' input variable ABSG). The defining equation is:

Eq. 2.106 $$ABSG = Ab/(l*[P])$$

where Ab is the absorbance measured in a spectrophotometer, l is the pathlength in cm, and [P] is the molar concentration of the chemical. The presence of the chemical in a natural water body increases the absorption coefficient (units /m) of the water from (a) to (a + (100 cm/m)(ln 10)(ABSG)[P]). The total rate of light absorption in the water body then becomes, by substitution into Eq. 2.105,

Eq. 2.107 $$Iw = (10)(Io/z)\{1-\exp(-D\{a + (100)(2.303)(ABSG)[P]\}z)\}$$

where D is the relative optical path in the water body (Eq. 2.101). The fraction of this light absorbed by the pollutant itself is:

$$\frac{(2.303)(100)(ABSG)[P]}{a + (2.303)(100)(ABSG)[P]}$$

and the rate of light absorption by the pollutant Ia, in E/liter/s, is:

$$\text{Eq. 2.108} \quad Ia = \frac{(2303.)(Io)(1-\exp(-D(a+230.3(ABSG)[P])z))(ABSG)[P]}{(a + 230.3(ABSG)[P])\ z}$$

At trace levels of the pollutant (EXAMS' operating range), by definition the quantity (230.3(ABSG)[P]) << a, and (a + 230.3(ABSG)[P]) can be approximated by the natural absorption coefficient of the water body, a. Equation 2.108 in these circumstances reduces to:

$$\text{Eq. 2.109} \qquad Ia = \frac{(1000)(2.303)(ABSG)\ Io\ (1-\exp(-Daz))}{(a)(z)}\ [P]$$

The quantity Ia/[P] is called the "specific sunlight absorption rate" of the pollutant, Ka (Zepp 1980).

Ka can also be computed from the average light intensity in any layer of the water body (Miller and Zepp 1979a). In this approach, the average light intensity Em (photons/cm2/s) is found by integration of Eq. 2.102 over the depth of the layer z, followed by division of the resulting integral by z:

$$\text{Eq. 2.110} \qquad Em = \frac{E(0)\ (1-\exp(-Daz))}{(D)(a)(z)}$$

where E(0) is the intensity at the top of the layer. Em (photons/cm2/s) can be converted to molar units (Im, E/cm2/s) via division by Avogadro's number:

$$\text{Eq. 2.111} \qquad Im = \frac{Em}{A} = \frac{E(0)}{A} * \frac{(1-\exp(-Daz))}{(D)(a)(z)}$$

which, taking Io = E(0)/A,

$$= \frac{1}{D}\ \frac{Io(1-\exp(-Daz)}{(a)(z)}$$

The term Io(1-exp(Daz)/az in this equation is embedded in Eq. 2.109; Ia and Ka can thus be computed from the average light intensity Im via the equivalent expressions:

Eq. 2.112 $$Ia = 2.303 * 1000\ (cm3/liter) * (ABSG)\ Im\ D\ [P]\quad ,$$

and

Eq. 2.113 $$Ka = 2303.\ (ABSG)\ Im\ D$$

Light absorption is a one-quantum process, thus Ia (E/liter/s) also gives the rate of electronic activation of the pollutant (M/s). Ka, the specific sunlight absorption rate, thus has units /s. If each photon absorbed by the chemical pollutant resulted in photochemical transformation of one molecule, Ka would amount to a pseudo-first-order rate constant for photolysis of the pollutant. This is seldom the case in solution-phase systems, however. The efficiency of the (secondary) photochemical transformation process is called the "reaction quantum yield" (EXAMS input parameter QUANTG), with (dimensionless) units of moles/Einstein. (Zepp (1978) has described procedures for measuring QUANTG of organic chemicals in dilute air-saturated aqueous solutions.) The rate of photochemical transformation of a pollutant is given by:

Eq. 2.114 $$d[P]/dt = (QUANTG)\ Ia = (QUANTG)\ Ka\ [P]$$

The quantity (QUANTG)(Ka) is the pseudo-first-order photolysis rate constant. Multiplication of this quantity by 3600 s/hr gives the photolytic contribution to the overall transformation rate constant K in Eq. 2.1.

Although the foregoing discussion has been phrased in terms of monochromatic light, the effect of spectral differences can be readily incorporated via integration or summation (in discrete wavebands) across the solar spectrum. The rate of photolysis of a synthetic organic compound thus can be computed from the absorption spectra and reaction quantum yields of the several ionic species of the chemical, via a coupling of these parameters to the (spectrally-dependent) behavior of light in natural waters (EXAMS' subroutine PHOTO2). Often, however, the absorption spectrum of a compound has not been quantified (although the spectral position of absorption maxima may be known). EXAMS provides an additional subroutine, PHOTO1, designed to accept measured photolysis rate constants as its primary input data. For example, Smith and coworkers (1978b) attempted to measure the absorption spectrum of Mirex, but the absorptivity was below the detection limit of their instrument (0.1 /cm/M). Experimental studies, conducted via continuous exposure of an aqueous solution of Mirex to ambient sunlight at Menlo Park, CA for a period of 6 months, showed that Mirex is photochemically reactive in aqueous solution with a pseudo-first-order rate constant of 3.7E-3 /day. (A pseudo-first-order rate constant determined via a brief experiment, for example at midsummer local noon, should be adjusted for annual mean intensity and daylength prior to entry in EXAMS.)

So long as the reaction mixtures absorb a negligible fraction of the ambient light (Im = Io), this observed rate constant (KDPo) is equivalent to:

$$KDPo = (QUANTG)\ Ka = 2303.\ (QUANTG)\ (ABSG)\ Io\ D$$

integrated across the solar spectrum. The average photolysis rate constant in a layer of appreciable depth (KDPz) is then

$$\text{Eq. 2.115} \qquad KDPz = KDPo * \frac{1 - \exp(-Daz)}{(D)(a)(z)}$$

where the absorption coefficient (a) for the water body is some appropriate single value. PHOTO1 also computes a correction term for effects of cloudiness and geographic latitude. EXAMS' input variable (KDPG, units /hr) is taken as the near-surface pseudo-first-order photolysis rate constant under cloudless conditions at a specified latitude RFLATG. RFLATG is expressed in degrees + tenths. For example, Menlo Park, California, is at 37 deg 27' N; EXAMS' input would be RFLATG = 37.4.

2.3.3.2 Light attenuation in natural waters

The attenuation of irradiance in natural waters is described by the diffuse attenuation coefficient or "K-function," K (Eq. 2.101), with units /m. The numerical value of K depends upon both the absorbance of the medium (a), and upon the relative optical path in the water body (D). The absorbance of a natural water body results from absorption of light by the water itself, plus absorption by green plants, dissolved organic matter (primarily humic materials), and suspended sediments. The optical path parameter D depends on the angle of incidence of the light source(s), and on forward scattering of the light within the water body itself.

2.3.3.2.1 Distribution functions (D) in natural waters

The optical parameter D is the mean optical path per unit vertical depth in the system; D may be called a "distribution function" as proposed by Priesendorfer (1958a, 1958b; quoted from Smith and Tyler 1976), or an "inverted value of an average cosine" where the average cosine is defined as a/K (Jerlov 1976). (The term "average cosine" originated from a generalization of the fact that the path length of the solar beam is given by the secant (1/cos) of the angle of refraction of the beam.) In the case of a collimated light beam incident normal to the water surface, D = 1.0. In the case of a completely diffused light field, D reaches its maximum value of 2.0 (Leighton 1961:24ff).

In the clearest natural waters, the distribution function is dominated to appreciable depths by the geometry of incident sky radiation and the solar beam. When the sun is in the zenith, the solar D = 1.0; D increases with increasing zenith angle. When the sun is near the horizon, D reaches a limiting value of about 1.5, because of refraction of the solar beam as it crosses the air-water interface. At low solar elevations, however, the underwater light field in the photochemically significant portion of the solar spectrum is dominated by contributions from diffuse skylight.

The collimating effect of transmission across the air-water interface reduces the distribution function for diffuse skylight from a D of 2.0 in the atmosphere, to a submarine value of about 1.19 (Poole and Atkins 1926, quoted from Hutchinson 1957:391). This value corresponds to an equivalent solar elevation of about 44 degrees. The total incident photochemically active irradiance (wavelengths < 370 nm) is dominated by skylight at solar altitudes less than 45 degrees, and irradiance at wavelengths < 330 nm is dominated by sky radiation at all solar elevations (Leighton 1961:23). A distribution function of 1.19 is thus probably an adequate approximation for the clearest natural waters.

In most natural waters, and in the deeper parts of clear waters, the radiance distribution approaches an asymptotic value in which forward scattering by suspended particles is balanced by light absorption, and the distribution coefficient attains a stable value. At shallow depths in natural waters containing scattering particles, D is usually larger than the value suggested by the solar elevation. For example, in the Baltic Sea and in the Mediterranean, D has been measured at 1.40 and 1.25, respectively (Hojerslev 1973, 1974; Jerlov and Liljequist 1938; quoted from Jerlov 1976:88). The corresponding solar beam D values were only 1.14 and 1.04 respectively, indicating a strong effect of particle scattering in these waters. Miller and Zepp (1979a) measured light scattering by 6 natural sediment suspensions. The distribution function ranged from 1.3 to 2.0, but showed little correlation with the suspension concentrations of the sediments (17 - 105 mg/L).

The distribution function for each element of the water body is an (environmental) input parameter to EXAMS. These parameters (DFACG) can be set at any value between 1.0 and 2.0. If an input value is <1 or >2, however, EXAMS resets the distribution function of the offending compartment to DFACG = 1.19.

2.3.3.2.2 Absorption coefficients (a) in natural waters

EXAMS computes separate values of the spectral absorption coefficients (a) for each sector of the water body. Absorption is computed from the sum of the contributions of water itself, plant pigments, dissolved organic carbon (primarily attributable to humic materials of molecular weight > 1000 (Mickle and Wetzel 1978)), and suspended sediments. Absorption coefficients for water itself, and the specific absorption coefficients for the other absorbing species, are given in Table 2.18. These values are not available for modification by the interactive user. The absorption coefficients can be modified by editing EXAMS' BLOCK DATA and recompiling the program.

EXAMS computes the total absorption coefficient (a, units /m) for each spectral interval in each water column compartment via Eq. 2.116:

Eq. 2.116 $a=WATETA+(PIGETA)(CHLG)+(DOCETA)(DOCG)+(SEDETA)(SDCHRG)$

The spectral specific absorption coefficients supplied with the program (PIGETA, DOCETA, SEDETA) are given in Table 2.18. The environmental concentrations of the absorbing species (CHLG, DOCG, and SDCHRG) are entered as part of the environmental data base for each water-column compartment of each ecosystem. These variables have dimensions (mg/L); they can be modified interactively.

Absorption by plant pigments is keyed to the concentration of total chlorophyll-like pigments (chlorophylls + pheopigments) in each sector of the water column (input varible CHLG, units mg/L). Under very eutrophic conditions, Chl "a" can attain 2 mg/L (Talling et al. 1973, quoted from Wetzel 1975:337). In oligotrophic alpine and arctic lakes, pigment concentrations can be as low as 0.001 mg/L (Wetzel 1975:334). Smith and Baker (1978b) determined the contribution of total chlorophyll-like pigments (CHLG) to the K-function of marine systems via regression analysis; the resulting spectral K values differed little from spectrophotometrically determined absorbance of phytoplankters. EXAMS' specific absorption coefficients (PIGETA in Eq. 2.116 and Table 2.18) were developed by division of Smith and Baker's (1978b) "k2" by an assumed average distribution function of 1.20.

EXAMS' specific absorption coefficients for DOC (DOCETA) were supplied by R.G. Zepp (unpublished data). These values (Table 2.18) were determined via analysis of samples from the Aucilla River, Florida, a natural water receiving stained drainage from freshwater wetlands. The Aucilla River data are probably fairly typical of the humic materials found as dissolved organic carbon (DOCG) in natural waters.

Light absorption by suspended sediments may vary across the solar spectrum, but interference by particle scattering has hampered investigation of this phenomenon. Miller and Zepp (1979a) determined both D- and K-functions for 331 nm light, via actinometer experiments conducted on a series of 6 natural sediment suspensions. The specific absorbance coefficient ((D/K)/[S], where [S] (i.e., SDCHRG) is the concentration of suspended sediments in mg/L) varied from 0.19 to 0.59, with a mean value of 0.34, /m/(mg/L). EXAMS includes a 39-element vector of specific sediment absorption coefficients; this vector is currently uniformly filled with a value of 0.34.

In the case of subroutine PHOTO1, the absorption spectrum of the compound is not available for coupling to the absorption spectrum of the water body. Subroutine PHOTO1 requires appropriate single absorption coefficients "a" (input parameter CMPETG). These values can be entered as part of the environmental data base. Each compartment of the ecosystem is then described by an individual element of EXAMS' vector CMPETG, with units /m. Alternatively, CMPETG can include (or be filled with) zero values; EXAMS then computes a value (or values) of CMPTEG via Eq. 2.116. The wavelength interval selected for this computation depends on the chemical data describing the compound. The chemical data base includes a variable (LAMAXG, nm) that can be used to specify the desired wavelength interval for computing "a" (i.e., CMPETG). The region of greatest overlap of the absorption spectrum of the chemical with the solar spectrum is perhaps the most appropriate value for LAMAXG. In many instances, however, only the spectral location of peak absorbance is known, in which case this value can be used for LAMAXG. If LAMAXG is outside the solar spectrum (that is, <296.25 nm or >825 nm), EXAMS computes CMPETG via Eq. 2.116 at 300 nm (interval 2 in Table 2.18). Input values of LAMAXG need not be restricted to the centers of the wavebands in Table 2.18; EXAMS selects the specific absorption coefficients for computing CMPETG via a matching of LAMAXG to the appropriate spectral intervals in the Table. For example, if LAMAXG = 306.5, EXAMS selects absorption coefficients from waveband 5 in Table 2.18; a LAMAXG of 442.2 selects waveband 23; etc.

2.3.3.3 Reaction quantum yields (QUANTG)

A photoactivated organic molecule can undergo a variety of secondary (thermal) transformations, including photoaddition and substitution reactions, cycloadditions, isomerizations and rearragements, and photofragmentations and eliminations (Turro 1978). The efficiency of photochemical processes is expressed in terms of the "quantum yield," that is, the number of moles of photochemical activity per mole of photons (Einsteins) absorbed. Photoactivated molecules are subject to numerous physical and chemical processes, and the efficiency of each of these processes can be expressed as a quantum yield (examples include the fluorescence quantum yield, phosphorescence quantum yield, quantum yield for formation of a specific product molecule, etc.) The quantum yield of significance for EXAMS is the "disappearance" quantum yield (input parameter QUANTG), that is, the number of moles of parent compound transformed to daughter products per mole of photons absorbed.

The (secondary) transformation processes often involve thermal reactions, and the disappearance quantum yield therefore can be somewhat temperature dependent. These thermal reactions are very fast, however, as they must be in order to compete with thermal reversion of the unstable intermediates to the original pollutant molecule. The activation energies of the thermal transformation reactions are on the order of only 1-2 kcal/mole, so EXAMS does not include an option for description of temperature effects on disappearance quantum yields.

Unlike vapor-phase photochemical reactions, the disappearance quantum yields of organic molecules in aqueous solution are usually independent of the wavelength of incident radiation, at least within the environmentally significant portion of the solar spectrum. This difference arises from the enhanced opportunity for energy transfer to the solvent in condensed-phase systems. In solution-phase irradiation, the rapid (radiationless) decay of excited molecules from second or higher electronic states, to their first excited state, normally precludes reaction from the higher states (Zepp 1978). Some organic dyes, stable under visible light but photochemically labile under UV, are notable exceptions to this rule. This phenomenon should be suspected when a 100+ nm gap is present in the compound's absorption spectrum. In such a case the assumed lack of wavelength dependence of QUANTG should be tested by experiments conducted in both absorbing regions of the spectrum. If necessary, the photochemically inactive section of the compound's absorption spectrum can be omitted from the input data (ABSG). Very small organic molecules, and some coordination compounds, can exhibit a wavelength dependence of QUANTG. The photochemistry of iron (II) cyanide complexes is one example of this phenomenon (Balzani and Carassiti 1970, quoted from Zepp 1978). Most small organic molecules in aqueous solution are photochemically unreactive in sunlight, however. The disappearance quantum yields used as input to EXAMS should in all cases be derived from experiments using wavelengths that are part of the environmentally relevant portion of the solar spectrum, rather than far UV (< 290 nm).

QUANTG can also be affected by the chemistry of the water solution itself. The quantum yields of the ionic species of an organic acid or base generally differ. This phenomenon leads to an apparent dependence of QUANTG on the pH of the medium. EXAMS allows for the entry of a separate value of QUANTG for each ionic species of the compound. This information can be deduced from a knowledge of the pK(s) of the compound, absorption spectra of its ionic species, and quantum yield experiments conducted at several pHs. For example, Zepp (1978) has described methods for determining disappearance quantum yields via comparison of the rate of transformation of a test pollutant P to that of a reference compound R, of known absorptivity ABSG(R) and quantum yield QUANTG(R). The method depends on a comparison of the slopes of the (pseudo-first-order) ln [P] and ln [R] disappearance curves over time, under irradiation at a selected wavelength (e.g., 313 nm). The reference compound serves to normalize the experiment for light intensity and the geometry of the photochemical apparatus. For a neutral molecule,

Eq. 2.117
$$\mathrm{QUANTG(P)} = \frac{\mathrm{SLOPE(P)}}{\mathrm{SLOPE(R)}} * \frac{\mathrm{ABSG(R)} * \mathrm{QUANTG(R)}}{\mathrm{ABSG(P)}}$$

The apparent QUANTG of an organic acid or base will depend on the pH of the system. For a fixed pH, Eq. 2.117 can be rewritten to include the ionization equilibria and separate absorptivites and quantum yields of the various ionic species of the pollutant P. For example, a monoprotic organic acid will distribute between its uncharged (SH2) molecule and its anion (SH-) (see Section 2.2.4) as:

Eq. 2.118
$$\mathrm{ALPHA(SH2)} = 1/(1 + (\mathrm{Ka})/\{\mathrm{H+}\})$$
, and

Eq. 2.119
$$\mathrm{ALPHA(SH-)} = (\mathrm{Ka}/\{\mathrm{H+}\})/(1 + (\mathrm{Ka})/\{\mathrm{H+}\})$$

where ALPHA is the fraction of the total pollutant present as each of the molecular species. Equation 2.117 then becomes

Eq. 2.120
$$\mathrm{ALPHA(SH2)} * \mathrm{ABSG(SH2)} * \mathrm{QUANTG(SH2)} + \mathrm{ALPHA(SH-)} * \mathrm{ABSG(SH-)} * \mathrm{QUANTG(SH-)} = \frac{\mathrm{SLOPE(P)}}{\mathrm{SLOPE(R)}} * \mathrm{ABSG(R)} * \mathrm{QUANTG(R)}$$

Suppose, for example, that P is a monoprotic organic acid whose pKa = 5.0. At pH 5, the compound would distribute equally between SH2 and the SH- anion. At pH 4.5, the compound would distribute as 76% SH2 and 24% SH-. Given, for example, ABSG of SH2 as 5000, and ABSG of SH- as 10000 at 313 nm, and experimentally determined values for the right side of Eq. 2.120 as 10 and 20 at pH 4.5 and 5.0, respectively; the quantum yields of the molecular species can be calculated via simultaneous solution of the equations:

(0.76)(5000)(QUANTG(SH2)) + (0.24)(10000)(QUANTG(SH-)) = 10

(0.50)(5000)(QUANTG(SH2)) + (0.50)(10000)(QUANTG(SH-)) = 20

giving a reaction quantum yield for the uncharged molecule of 1.5E-4, and QUANTG(SH-) = 3.9E-3.

Zepp and Baughman (1978) have discussed the effect of other dissolved species on the direct photolysis of synthetic organic molecules. Dissolved oxygen in some instances "quenches" photochemical reactions via energy transfer from a pollutant molecule to the oxygen molecule at the expense of transformation pathways. Disappearance quantum yields should be determined in air-saturated pure water to allow for this effect; EXAMS does not include an explicit algorithm to make allowances for varying dissolved oxygen concentrations. (Sunlit waters are very rarely anaerobic.) Photochemical reactions with dissolved nucleophilic species such as hydroxide, chloride, bromide, and sulfide can change the reaction quantum yield of a pollutant from the value determined in in pure water system. The concentrations of these species in natural fresh waters are, however, typically much too small for them to compete with nucleophilic displacements by water itself. In marine systems, chloride and bromide occur at concentrations (0.6 and 0.001 Molar, respectively) high enough to compete, in principle, with water.

Some organic compounds that are not photoreactive in pure water are photoactive when complexed with metal ions. For example, NTA and EDTA are photochemically activated by complexation with iron (III). Photoactive co-dissolved substances (e.g., dissolved humic materials) can also mediate photoreactions of pollutant chemicals via direct energy transfer to the pollutant molecule, or by generation of reactive intermediates (e.g., singlet oxygen). These phenomena are properly termed "indirect" or "sensitized" photolyses, however, as opposed to the "direct" phototransformations that are the subject of this Section.

2.3.3.4 Absorption spectra (ABSG)

The absorbance of organic acids and bases in aqueous solution varies with pH, as a result of differential light absorption by the neutral molecule and its ions. The rate of photolytic transformation of an organic acid or base in natural waters thus depends on the pH of the system. EXAMS' computations (in Subroutine PHOTO2) are keyed to the species-specific absorption spectra of the pollutant chemical (uncharged parent molecule and its ionic species), measured in pure water. Subroutine PHOTO2 links the average spectral solar intensities in each layer of the water body to the absorption spectra of the compound, and thereby computes a value of Ka (Eq. 2.113) for each dissolved molecular species. Subroutine PHOTO2 is invoked by another subroutine (FIRORD) whose primary task is to merge environmental and chemical data into the final pseudo-first-order format (Eq. 2.1) needed for efficient computations.

EXAMS' only dynamic state variable is the total concentration of pollutant in each ecosystem segment, referred to the aqueous phase of the compartment. The fraction of this total concentration present as each molecular species is computed via the equilibrium ionization and sorption distribution coefficients ALPHA (Section 2.2.4). Subroutine FIRORD, once in possession of Ka values for the several ionic species, computes the contribution of each to the total pseudo-first-order direct photolysis rate constant via the expression (compare Eq. 2.114):

ALPHA(I) * QUANTG(I) * Ka(I)

where the subscript (I) refers in turn to each of the ionic species.

This computational loop is actually iterated 3 times for each ionic species, because EXAMS incorporates the effects of sorption to sediments and biota via a set of 3 values of QUANTG for each ionic species. In other words, for each ionic species I, EXAMS computes the total contribution of that species to the overall direct photolysis rate constant by fixing the value of I, and summing the expression:

ALPHA(I,K) * QUANTG(I,K) * Ka(I)

over the K=1 (dissolved), K=2 (sediment sorbed), plus K=3 (biosorbed) forms of the compound in each sector of the ecosystem. The mechanics of this computation allow the user to control the photoreactivity of sorbed molecules via the entries in the QUANTG chemical input vectors.

Sorption of the pollutant to suspended sediments and to biota can induce complex changes in both the light absorption spectra and the reaction quantum yields of the compound, and can "protect" the molecule from exposure to sunlight via migration or dissolution into the (darkened) interior of sediment particles. EXAMS' first-order evaluations use the quantum yield parameter (QUANTG) as a mechanism for approximating the effects of sorption on the photoreactivity of pollutant chemicals; the phenomena involved are discussed in greater detail in Section 2.3.3.5.

In order to compute the effects of pH on light absorption and on photolytic rate constants, EXAMS requires a specific absorption spectrum (ABSG vector) for each (dissolved) molecular species of the pollutant chemical. These absorption spectra can be deduced from the pK(s) of the compound and the absorption spectra of aqueous solutions of the chemical, measured at several pHs. The procedure is analogous to that described for QUANTG in Section 2.3.3.3. For example, Smith and coworkers (1978b) measured the absorption spectrum of p-Cresol at pH 5.1, 7.0, and 8.9 (Table 2.19). Para-cresol is a weak organic acid (pKa = 10.2); at pH 5.1, 7.0, and 8.9 the anion is present as only 0.00079, 0.063, and 4.77 percent of the total concentration. The observed spectra (Table 2.19) clearly indicate that the anion is the more strongly absorbing species.

Table 2.19. Absorption spectra of p-Cresol in pure water

Waveband Center,	Spectral Absorption Coefficients (/cm/M)					
nm	pH 5.1*	pH 7.0*	pH 8.9*	(SH2)+	(SH-)+	pH 7.0#
297.5	14	18	193	14	3767	16
300.0	3.8	7.2	173	3.8	3551	6.0
302.5	2.4	3.8	150	2.4	3097	4.4
307.5	0	2	92.6	0	1941	1.2
310.0		2	63.5		1331	0.8
312.5		1	40.3		845	0.5
315.0		0	24.1		505	0.3
317.5			13.0		272	0.2
320.0			6.2		130	0.08
323.1			3.8		80	0.05
330.0			0			

* Spectra measured at pH 5.1, 7.0, and 8.9 by Smith et al. 1978b

+ Spectra of uncharged (SH2) molecule and p-Cresol anion derived via Eq. 2.121

# Absorption at pH 7.0 predicted via Eq. 2.121, pKa of 10.2, and absorption coefficients of (SH2) and (SH-) molecular species.

The observed absorption coefficient at any fixed wavelength is the sum of absorbance attributable to the uncharged (SH2) molecule, plus that attributable to the anionic (SH-) species. Denoting the observed absorption coefficient as ABS, this sum can be expressed algebraically:

Eq. 2.121 ABS = ALPHA(SH2) * ABSG(SH2) + ALPHA(SH-) * ABSG(SH-)

This equation can be used to estimate the separate absorbances of the SH2 and SH- molecules. For example, at 297.5 nm, for pH 7.0:

$$18 = (0.999369)\ ABSG(SH2) + (6.31E-4)\ ABSG(SH-)$$

and at pH 8.9,

$$193 = (0.952)\ ABSG(SH2) + (0.0477)\ ABSG(SH-)$$

Simultaneous solution of these equations yields ABSG(SH2) = 15.6 and ABSG(SH-) = 3734.

The uncharged molecule is present as 99.9992% of the total concentration at pH 5.1, so the pH 5.1 spectrum is perhaps the best experimental measure of ABSG(SH2). Taking this to be so, the absorption spectrum of the (SH-) anion can be calculated from the pH 8.9 spectrum via Eq. 2.121. For example, at 297.5 nm,

$$193 = (0.952)(14) + (0.0477)\ ABSG(SH-)$$

gives ABSG(SH-) = 3767. The accuracy of this procedure can be tested by using Eq. 2.121 to predict absorbance of the solution at pH 7.0:

$$(0.999369)(14) + (6.31E-4)(3767) = 16\ (/cm/M)$$

as compared to the experimental value of 18 /cm/M. The computed absorption spectra of the uncharged SH2 molecule and the SH- anion of p-Cresol are also shown in Table 2.19, with the projected absorption coefficients at pH 7.0. The absorption spectra of the individual molecules are the appropriate data for entry into EXAMS' chemical data base (input vectors ABSG).

2.3.3.5 Effects of sorption to suspended sediments and biota

The effects on direct photolysis of sorption to suspended sediments and biota are incorporated into EXAMS via separate disappearance quantum yields (QUANTG) for the sorbed forms of each dissolved species (SH2, SH-, etc.) of the compound. Although sorption can produce subtle and complex changes in the photochemistry of pollutants, light extinction by suspended particulate matter, and capture of sorption-prone chemicals by bottom sediments, relegate the effects of sorption to a secondary role. It cannot simply be assumed, however, that sorption inevitably "protects" a chemical from direct interaction with solar radiation, so EXAMS allows for alternatives to this assumption via the QUANTG chemical input vector.

The "sorption" process includes adsorption of a chemical onto particle surfaces, dissolution of uncharged species into suspended organic materials, and migration into the interior of particles via diffusion along pore channels. The particle microenvironment is often very different from that of the surrounding aqueous milieu. For example, the surface acidity of clay minerals can result in protonation of organic bases beyond that predicted by solution-phase pH and pK (Karickhoff and Bailey 1976). This effect can, at least in principle, be represented via EXAMS' separated partition coefficients for the ionic species of a pollutant (Section 2.2.2). The extent of the sorption/protonation process is influenced, however, by particle size, interactions with the solution-phase carbonate system, and inorganic cations adsorbed on the clay surface. These complexities, and the fact that mineral clays constitute a varying proportion of natural sediments, restrict EXAMS to the phenomenological approach described in Section 2.2.2. The photoreactivity of an organic acid or base can be affected by ionic speciation at the surface of adsorbent particles. Bailey and Karickhoff (1973) demonstrated this effect via its converse: these authors showed that UV spectroscopy can be used to monitor surface acidity of clay minerals via the shift in the absorption spectrum of adsorbed organic bases from that of the uncharged, to the protonated, molecular species.

The dissolution of neutral organic pollutants into suspended organic matter or surface organic films also removes the chemical from aqueous solution to a very different microenvironment. This organic microenvironment may alter the absorption spectrum, quantum yields, and photochemical reactions of a sorbed molecule, for organic sorbents usually differ from water in both refractive index and polarity. A change in the refractive index of the absorbing medium implies changes in spectral radiation density (erg/cm3/unit frequency range) in the medium, and therefore in the apparent absorption spectrum of a pollutant chemical. Although the effects of such phenomena can be computed in some cases (Strickler and Berg 1962), the heterogeneity of natural suspended organic matter defies description. Particle size distribution (i.e., light extinction in the interior of the particle) would also affect the average radiation density experienced by a sorbed-phase pollutant.

In addition, reaction conditions within a suspended particle microenvironment must differ from those of aqueous solution; these differences can alter the reaction quantum yields and the kinds of photochemical products that result from irradiation of the system (Miller and Zepp 1979b). Suspended sediments may also retard sorbed-phase photoreactions by quenching excited states of the molecule, and may enhance photoreaction via indirect processes or "sensitized" reactions. Possible indirect reactions include the production of excited states or free radicals via irradiation of the organic matrix of the suspended particles, and photoelectric excitation of semiconductors, such as TiO_2, which are a common constituent of many natural sediments (Oliver, Cosgrove, and Carey 1979).

A few phenomenological investigations of the effects of natural suspended sediments on photochemical kinetics have appeared in the literature; the complexity of the phenomena has led their authors to describe their findings via apparent effects on reaction quantum yields. Oliver, Cosgrove, and Carey (1979) compared the effect of purified TiO_2 semiconductor to the photochemical efficacy of Ti ores (ilmenite and rutile) and natural river suspensoids. Although purified TiO_2 was an efficient photochemical catalyst, the Ti ores and the natural sediments alike simply suppressed the photochemistry of the test materials via competitive light absorption. Miller and Zepp (1979b), from studies of the photolysis of DDE and m-trifluoromethylpentadecanophenone (TPP) in natural suspended sediments, concluded that the sediment microenvironment is similar to a saturated hydrocarbon solvent. These authors reported an apparent increase in the disappearance quantum yield of sorbed DDE to 1.5 times its value in aqueous solution, and a factor of 2 to 6 decrease in the apparent quantum yield of TPP. Both results were consistent with the behavior of these compounds in organic solvents. Miller and Zepp (1979a) concluded that the competitive absorption of light by suspensoids is nonetheless the dominant effect of suspended particles on photolysis in natural waters.

2.3.3.5.1 Simulation analysis of sorption effects on direct photolysis

Photolytic transformation of pollutant chemicals is an important process in many aquatic systems, most especially when photochemical transformation is the only degradation process capable of limiting organism exposures under environmental conditions. This process is critically dependent on competitive light absorption by suspended materials, and on the effects of sorption on the availability of a pollutant to photochemical processes.

In a natural water body, capture of a pollutant by benthic sediments removes the compound to a photochemically inactive (dark) sector of the ecosystem. The net photochemistry of a pollutant chemical thus depends on solution- and sorbed-phase photoreactivity, competitive light absorption by suspensoids, and capture of the pollutant by the benthic subsystem. The interactions among these processes can be explored via EXAMS. For the example simulations, the ecosystem was a small (1 ha) static pond, 2 m deep, with a 1 cm active benthic subsystem of bulk density 1.75 g/cc and water content 150%. The example compound had a near-surface halflife of 1 hour in solution (KDPG = 0.6931, QUANTG(1,1) = 1.0), but was a full order of magnitude more photoreactive when sorbed with suspended sediments (QUANTG(2,1) = 10.0). The distribution function (DFACG) was taken as 1.20; EXAMS used the sum of light absorption by water itself (at 300 nm), plus the absorbance attributable to suspended sediments, to compute the average light intensity in the water column (Eq. 2.115). Systematic changes in the partition coefficient of of the chemical (KPS) and the concentration of suspended sediments (SDCHRG) then were used to elucidate their net effect on the photochemistry of the compound, under conditions most favorable for enhancement of phototransformation kinetics by sorption.

The results of simulations using a suspended sediment concentration of 10 mg/L and varying partition coefficients (0 - 1.E6 L/kg) are given in Table 2.20. These results are given in terms of pseudo-first-order halflives for the water column subsystem alone, and for the entire pond ecosystem. (The whole-system halflives assume that the rate of transport from the benthic subsystem into the water column does not limit the rate of photochemical transformation of the compound.) Under these environmental conditions, less than 1% of the compound in the water column is in the sorbed state for a partition coefficient less than 1000 L/kg. When the partition coefficient is greater than 1000, however, more than 85% of the resident material is captured by the (dark) benthic subsystem. The system-level halflife of the compound increases steadily with increasing Kp, despite the greater photoreactivity of the sorbed material.

The effect of competitive light absorption by suspended materials was examined by fixing the partition coefficient at 100 L/kg, and systematically increasing the concentration of suspended sediments from 0 to 10,000. mg/L (Table 2.21). In this case, light absorption by the suspended sediments rapidly increased the photochemical halflife of the compound. This effect overwhelmed the enhanced photoreactivity of the sorbed material, despite the fact that more than half of the total compound in the system resided in the water column (at steady state).

Table 2.20. Effect of partition coefficient Kp (liters/kg) on net photoreactivity when suspended sediment concentration = 10 mg/L*

Kp, L/kg	Percent dissolved in water	Percent captured by benthos	Pseudo-First-Order Halflives, hours Water Column	Whole System
0.	100.	0.29	8.50	8.52
1.	100.	0.87	8.50	8.57
10.	100.	5.8	8.49	9.01
100.	99.9	36.9	8.42	13.4
1000.	99.0	85.2	7.80	52.9
10000.	90.9	98.2	4.68	253.
100000.	50.0	99.7	1.55	452.
1000000.	9.09	99.8	0.93	492.

* Average light intensity in water column 11.8% of surface value

Table 2.21. Effect of suspended sediment concentration [S] on net photoreactivity when partition coefficient Kp = 100 liters/kg

[S], mg/L	Percent dissolved in water	Percent benthic capture	I(z)/I(0) (Average) %	Pseudo-First-Order Halflives, hours Water Column	Whole System
0.	100.	36.96	84.8	1.18	1.87
1.	100.	36.96	59.3	1.68	2.67
10.	99.9	36.93	11.8	8.42	13.4
100.	99.0	36.73	1.22	75.2	119.
1000.	90.9	34.77	0.12	449.	688.
10000.	50.0	22.67	0.012	1484.	1918.

The system-level pseudo-first-order halflife indicates the outcome of the interaction between competitive light absorption by suspended materials, capture of the compound by bottom sediments, and enhanced photoreactivity in the sorbed state. Table 2.22 gives the system-level photochemical halflife of a compound that is 100 times more reactive in the sorbed, than in the dissolved, state, for a range of Kp and sediment concentrations unlikely to be exceeded in nature. As compared with the 1.18 hour halflife of the unsorbed, clean-water baseline, an increase in sorption leads to a net suppression of the rate of photochemical transformation of the compound in all cases, despite the uniquely (and unrealistically) favorable conditions assumed for the analysis. In sum, the effects of residence in the sorbed state on photoreactivity are of secondary importance, and can be adequately summarized via a simple descriptive parameter (QUANTG), in the context of a first-order evaluation.

Table 2.22. Effect of suspended sediment concentration (mg/L) and partition coefficient (Kp, liter/kg) on system-level pseudo-first-order photochemical halflife (hours) when sorbed chemical is 100 times more reactive than dissolved species

Kp,	Suspended Sediment Concentration, mg/L					
liter/kg	0	1	10	100	1000	10000
0.	1.18	1.69	8.52	82.2	819.	8182.
1.	1.19	1.70	8.57	81.8	749.	4157.
10.	1.25	1.79	8.93	79.1	437.	861.
100.	1.87	2.65	12.3	65.4	125.	209.
1000.	8.06	10.5	29.1	51.7	63.3	137.
10000.	69.9	50.0	45.9	49.0	56.6	130.
100000.	689.	89.6	49.2	48.6	55.9	129.
1000000.	6876.	97.4	49.6	48.6	55.8	129.

The effects of sorption to organic slicks at the air-water interface are not included in EXAMS for similar reasons:

Although the concentration in the slick can be large, the total fraction of the pollutant resident in the film is probably too small to have much effect on the system-wide kinetics of pollutant chemicals (Zepp and Baughman 1978).

EXAMS represents the photochemical effects of sorption to suspended sediments, and to biota, via separate entries in the QUANTG vectors. Note that these vectors represent the effect of residence in the biosorbed state on the direct photolysis of the pollutant; they are not intended to represent photosensitization or photobiological transformation of pollutants by phytoplankton. Although qualitive studies have indicated that this pathway exists, as yet a quantitative basis for predicting its magnitude and importance in natural systems has not been developed (Zepp 1980).

2.3.3.6 Near-surface solar beam and sky irradiance (input WLAMG)

The spectral light field is entered into EXAMS as a vector ("WLAMG") of 39 photon irradiances. WLAMG is the total (solar beam plus skylight) irradiance under clear (cloudless) conditions, just below the air-water interface (that is, after subtracting reflected light from the light incident on the surface). EXAMS corrects the input irradiance for effects of cloud cover via Buttner's (1938, cited from Zepp 1980) empirical relationship:

Eq. 2.122 WLAMG <--- WLAMG * (1 - 0.056*(CLOUDG))

The cloudiness (EXAMS' input scalar CLOUDG) term is the average sky cover in tenths, with a range from 0 (clear sky) to 10 (full cover).

Clear-sky irradiance at the earth's surface depends on latitude, site elevation, atmospheric turbidity and water vapor content, and the ozone content of the stratosphere (Leighton 1961). EXAMS' environmental WLAMG vector can be developed via site-specific measurements, or via estimates appropriate to the regional geography of an evaluative ecosystem type. Computational methods for estimating spectral irradiance have been explored by a number of authors (e.g., Leighton 1961; Green, Sawada, and Shettle 1974; Green, Cross, and Smith 1980; Green and Schippnick 1980; Dozier 1980). Irradiance spectra are often computed or measured in energy units. These spectra can be converted to photon irradiances via Planck's law. For example, given an energy spectrum ("Es") in uwatts/cm2/nm, WLAMG in photons/cm2/sec/N nm can be computed from:

Eq. 2.123 WLAMG = Es * 5.047E9 * LAM(nm) * N(nm)

where LAM is the wavelength of the incident radiation, and

$$1.E\text{-}6\ \frac{J/s}{uWatt} * \frac{1.E\text{-}9\ (m/nm)}{6.6262E\text{-}34\ (J\ s) * 2.99\ (m/s)} = 5.047E9$$

At 297.5 nm, for example, the appropriate conversion factor is:

WLAMG(1) = Es * 5.047E9 * 297.5 * 2.5 = 3.754E12 * Es

Zepp and Cline (1977), using a computer program ("SOLAR") available on request from those authors, calculated photon scalar irradiance ("W") at the 39 wavelength intervals adopted for EXAMS. Their report gave "midseason," "midday" spectral irradiance at 40 degrees N latitude. For EXAMS, these values must be reduced by a daylength factor and via sinusoid averaging over the photoperiod (i.e., multiplied by 2/3.14). Summer and winter photon irradiances ("W" values quoted from Zepp and Cline 1977), and yearly mean values, are shown in Table 2.23. The WLAMG vector given in this table is supplied with the nominal environmental definition distributed with the EXAMS software. Note that the bandwidths of the input wavebands, for wavelengths longer than 323.1 nm, are all per 10 nm. This waveband size does not correspond to the computational wavebands for intervals 29-39 (i.e., wavelengths > 490 nm; see Table 2.18). EXAMS expands the wavebands to their full computional bandwidth internally. For example, the input datum for interval 39, centered at 800 nm, is increased by a factor of 5 to expand the input WLAMG (/10 nm) to the full 50 nm computational bandwidth.

Subroutine PHOTO1 begins from near-surface precomputed photolysis rate constants (KDPG), and thus does not use the spectral irradiance vector WLAMG in its computations. PHOTO1 adjusts KDPG via a cloudiness correction (Eq. 2.122), and also corrects KDPG for the geographic translation from the latitude at which each KDPG was measured (RFLATG) to the latitude of the ecosystem (LATG). The correction term is computed from the total annual solar + sky radiation received at latitudes RFLATG and LATG. Ground-level radiation was computed as a function of latitude at 10 degree intervals via procedures described by List (1966) using an atmospheric transmission coefficient of 0.90. Estimated total radiation increased from 1.038E5 cal/cm2/yr at the pole, to 2.744E5 ly/yr at the equator. Regression of the (8) estimates on:

$$Y = a + b \cos(2L)$$

where L is the latitude in radians, yielded a = 1.917E5, b = 8.705E4, and accounted for 99.7% of the variation in total irradiance (Y) with latitude. In subroutine PHOTO1, the correction term for KDPG is computed as:

$$\mathrm{KDP} \longleftarrow \mathrm{KDPG} * \frac{a + b \cos (0.0349\ \mathrm{LATG})}{a + b \cos (0.0349\ \mathrm{RFLATG})}$$

For example, for a rate constant measured at the equator and a polar ecosystem,

$$\mathrm{KDP} \longleftarrow \mathrm{KDPG} * \frac{a + b \cos (0.0349 * 90)}{a + b \cos (0.0349 * 0)} = 0.38(\mathrm{KDPG})$$

This procedure is based on total solar energy input, and thus may underestimate the latitude dependence of photochemical transformation of pollutants that absorb sunlight most strongly at wavelengths < 320 nm.

2.3.3.7 Input data and computational mechanics -- Summary

Subroutine PHOTO1 was designed to evaluate chemicals whose absorption spectrum has not been quantified. Its primary input datum, KDPG, is a vector of pseudo-first-order photolysis rate constants. A separate value of KDPG can be entered for each existing ionic species (SH2, SH3+, etc.). KDPG is assumed to apply to near-surface waters, under cloudless conditions and full-day average solar irradiance. EXAMS adjusts the rate constant for light extinction in the water column , effects of cloud cover, and deviation of the latitude of the system (LATG) from the latitude at which the rate constant was measured (RFLATG).

Each value of KDPG is paired to 3 elements of the QUANTG matrix of disappearance quantum yields. QUANTG(1,k) is the disappearance quantum yield of the aqueous dissolved molecule(s) ("k" the number of the ionic species, where k = 1 denotes the uncharged (SH2) molecule, k = 2 is the (SH3+) cation, 3 is (SH4++), 4 is (SH-), and 5 is (S=)). Usually for PHOTO1 this parameter is set to a dummy unit value, but should the true quantum yield of the compound be known, a near-surface Ka (Eq. 2.113) can be loaded via KDPG, and the observed quantum yield(s) can be entered via QUANTG. QUANTG(2,k) and QUANTG(3,k) specify the quantum yields of the sediment-sorbed and biosorbed forms of each ionic species of the compound. These parameters allow for entry of known sorption effects on photolysis rate constants, and in any case allow the user to relax the assumption that sorption "protects" the compound from photoreactions.

Table 2.23. Sample input spectral irradiance (WLAMG) for EXAMS

No.	Waveband Center, nm	Input Width N, nm	Spectral Irradiance, photons/cm2/sec/N nm Summer*	Winter*	WLAMG+
1	297.5	2.5	6.47E+11	0.00E+00	8.91E+10
2	300.0	"	2.19E+12	6.01E+10	3.38E+11
3	302.5	"	6.57E+12	3.00E+11	1.11E+12
4	305.0	"	1.63E+13	1.39E+12	2.99E+12
5	307.5	"	2.74E+13	3.69E+12	5.40E+12
6	310.0	"	4.44E+13	6.98E+12	8.84E+12
7	312.5	"	6.43E+13	1.45E+13	1.38E+13
8	315.0	"	8.36E+13	2.22E+13	1.85E+13
9	317.5	"	1.03E+14	2.96E+13	2.33E+13
10	320.0	2.5	1.21E+14	4.08E+13	2.81E+13
11	323.1	3.75	2.26E+14	7.40E+13	5.21E+13
12	330.0	10.0	7.62E+14	2.79E+14	1.81E+14
13	340.0	"	8.75E+14	3.41E+14	2.11E+14
14	350.0	"	9.38E+14	3.63E+14	2.26E+14
15	360.0	"	1.00E+15	3.83E+14	2.41E+14
16	370.0	"	1.12E+15	4.18E+14	2.68E+14
17	380.0	"	1.24E+15	4.50E+14	2.94E+14
18	390.0	"	1.48E+15	6.46E+14	3.66E+14
19	400.0	"	2.12E+15	9.31E+14	5.26E+14
20	410.0	"	2.79E+15	1.23E+15	6.92E+14
21	420.0	"	2.87E+15	1.27E+15	7.12E+14
22	430.0	"	2.77E+15	1.23E+15	6.88E+14
23	440.0	"	3.27E+15	1.46E+15	8.14E+14
24	450.0	"	3.68E+15	1.64E+15	9.17E+14
25	460.0	"	3.72E+15	1.67E+15	9.27E+14
26	470.0	"	3.84E+15	1.72E+15	9.59E+14
27	480.0	"	3.94E+15	1.77E+15	9.83E+14
28	490.0	"	3.72E+15	1.68E+15	9.30E+14
29	503.75	"	3.80E+15	1.71E+15	9.49E+14
30	525.0	"	4.01E+15	1.81E+15	1.00E+15
31	550.0	"	4.18E+15	1.88E+15	1.05E+15
32	575.0	"	4.23E+15	1.90E+15	1.06E+15
33	600.0	"	4.27E+15	1.92E+15	1.07E+15
34	625.0	"	4.28E+15	1.96E+15	1.08E+15
35	650.0	"	4.29E+15	1.99E+15	1.08E+15
36	675.0	"	4.27E+15	2.00E+15	1.08E+15
37	706.25	"	4.22E+15	2.00E+15	1.07E+15
38	750.0	"	4.04E+15	1.93E+15	1.03E+15
39	800.0	10.0	3.87E+15	1.87E+15	9.88E+14

* Summer and Winter irradiances are "midseason, midday" values from Zepp and Cline 1977

+ WLAMG computed from daylength and sinusoidal (2/3.14) average of (4) seasonal midday irradiances

The computations executed by subroutine PHOTO1 are inherently less precise than wavelength-specific computations based on the chemical's absorption spectrum (PHOTO2), because PHOTO1 cannot evaluate the effects of spectrally differentiated light extinction in the water column. PHOTO1 is, however, useful for photoreactive compounds with absorbances too small to measure using current techniques.

Subroutine PHOTO2 couples the absorption spectra of the compound (ABSG(1-39,k)) to the irradiance spectrum incident on the water body (WLAMG). The QUANTG matrix in this case contains measured disappearance quantum yields; its use in EXAMS is in all other respects (effects of sorption, etc.) identical to the use described for subroutine PHOTO1.

Both photolysis subroutines operate on the incident light field to compute the average light intensity in each compartment of the ecosystem. (In PHOTO1, the incident light field has a nominal value of 1.0, because KDPG has built into it the clear-sky irradiance at latitude RFLATG.) PHOTO1 uses a spectral composite light absorption coefficient for each sector of the water body (CMPETG); PHOTO2 computes the absorption coefficient for each spectral waveband (Table 2.18) from the pigment (CHLG), dissolved organic carbon (DOCG), and suspended sediment (SDCHRG) concentrations in each compartment (Eq. 2.116).

The water column ("E" and "H" compartment types) can be subdivided into as many horizontal slices as seems appropriate for a particular water body. EXAMS traces light extinction vertically through the slices by computing irradiance at the bottom of each compartment, as well as the average irradiance used for computing photolysis rate constants. When the (J-1) compartment is another E or H segment, irradiance at the bottom of the (J-1) compartment is taken as the starting point for irradiance computations in the current (J) sector. This scheme will fail, however, if the system definition rules given in Section 2.3.1.1 are disregarded.

An example of a logical, but improper, segmentation scheme is shown in Figure 2.5a. Calls to EXAMS' photolysis subroutines are executed in compartment order. For this ecosystem, the first call computes photolysis in compartment 1, a (L)ittoral water column compartment. The incident light field at the air-water interface is identified as the light intensity at the top of the compartment, and EXAMS computes both average light intensity and irradiance at the bottom of compartment 1. Compartment 2 is a (B)enthic compartment;

```
+--------------------------------------------------------------+
|                                                              |
|   +-------------------------------------------------------   |
|   |       |                                                  |
|   |  L 1  |                                                  |
|   +-------+               E 3                                |
|   |  B 2  |\                                                 |
|   +-------+ \                                                |
|           |  +-------------+------------------------------   |
|            \     B 4       |\                                |
|             +--------------+ \                               |
|                            |  \                              |
|                             \  \        H 5                  |
|                              \  \                            |
|                               \  +------------------------   |
|                                \        B 6                  |
|                                 +-------------------------   |
|                                                              |
+--------------------------------------------------------------+
```

a. Improper segmentation: incomplete vertical definition.

```
+--------------------------------------------------------------+
|                                                              |
|   +-------------------------------------------------------   |
|   |       |                |                                 |
|   |  L 1  |                |                                 |
|   +-------+      E 3       |                                 |
|   |  B 2  |\               |            E 5                  |
|   +-------+ \              |                                 |
|           |  +-------------+------------------------------   |
|            \     B 4       |\                                |
|             +--------------+ \                               |
|                            |  \                              |
|                             \  \        H 6                  |
|                              \  \                            |
|                               \  +------------------------   |
|                                \        B 7                  |
|                                 +-------------------------   |
|                                                              |
+--------------------------------------------------------------+
```

b. Proper segmentation: complete vertical definition.

Figure 2.5. Examples of proper and improper vertical structure.

EXAMS simply sets the photolysis rate to 0 and does not call a photolysis subroutine. Upon reaching compartment 3, EXAMS checks the compartment type of the (J-1) compartment. As compartment 2 is neither E nor H, the incident light field is used to start the computations. (Note that the test is based on compartment types "E" and "H" only; (L)ittoral water column compartments thus should not be horizontally subdivided.) A photolysis subroutine is not invoked for (B)enthic compartment 4. When EXAMS now calls for irradiance computations for the (H)ypolimnion compartment (5), an error occurs. EXAMS inspects (J-1) compartment 4, finds it to be (B)enthic, and starts its computations for the hypolimnion using the surface incident light field, rather than intensity at the bottom of the epilimnion.

The proper system definition is shown in Figure 2.5b. In this case, upon initiation of computations for the hypolimnion (now numbered 6), EXAMS finds that the (J-1) compartment (5) is an (E)pilimnion segment. The light intensity at the bottom of compartment 5 (internal variable BOTLIT in PHOTO1, BOTLAM(1-39) in PHOTO2) is retrieved and used to start the irradiance computations for the hypolimnion.

EXAMS reports the average light intensity in each sector of the ecosystem as part of its "canonical profile" of the system. These reports are given as a percentage of the light field incident on the water body. The numerical value of this quantity can vary with the chemistry of the compound. For a chemical for which photolysis is computed via the KDPG vector (PHOTO1), the average light intensity is governed by CMPETG alone, but CMPETG can vary with LAMAXG. For a chemical for which photolysis is computed via the absorption spectrum (PHOTO2), the reported average light intensity is based only on that portion of the solar spectrum in which the compound absorbs radiation. Different chemicals thus experience a different reduction in total radiant intensity within the same waterbody.

For organic acids and bases, the apparent average light can be variously reported, depending upon which ionic species is evaluated at the first call to PHOTO1 or PHOTO2. For example, given a chemical with non-zero ABSG vectors for SH2 and SH-, the reported average intensity would be based upon the SH2 (first called) absorption spectrum, although a fuller (or reduced) portion of the solar spectrum might be used to compute photolysis of the SH- anion. For an amphoteric compound, if the SH2 molecule were described via KDPG, and the SH4+ and SH- ions were described via their absorption spectra, EXAMS would report average light levels based on the absorption spectrum of SH4+. This phenomenon arises from an interaction among the photolysis subroutines. In this case, the uncharged (SH2) molecule is evaluated first via subroutine PHOTO1, and EXAMS' internal variable (LIGHTL) that is reported in the "canonical profile" is computed from CMPETG. When PHOTO2 is called for evaluation of

SH4+, however, LIGHTL is recomputed over the part of the solar spectrum in which SH4+ absorbs light. During the third set of computations (SH- in PHOTO2), LIGHTL is not recomputed. If an S= (k=5) anion had been described via KDPG, the call to PHOTO1 would not reset LIGHTL, for PHOTO1 would have already executed this computation for the current compartment and will not repeat it.

In sum, it should be recognized that the average light intensity reported in EXAMS' "canonical profile" of the ecosystem results from interaction between the chemistry of the synthetic compound and properties of the ecosystem. This output provides a sense of the effect of competitive light absorption in the water body on photolysis of the compound, but it usually should not be interpreted as an intrinsic property of the ecosystem itself.

2.3.4 Specific Acid, Specific Base, and Neutral Hydrolysis

Many organic compounds react directly with water in the aqueous solvent system. In addition, water dissociates into hydronium and hydroxide ions, and the concentrations of these subsidiary species often affect the rates of chemical transformations. EXAMS includes kinetic constants for three kinds of hydrolytic pathways: specific-acid (H_3O^+) catalyzed, neutral hydrolysis, and specific-base (OH^-) catalyzed transformations.

The breakdown of esters to yield a carboxylic acid and an alcohol is a convenient example of hydrolytic transformations. The overall reaction is:

Eq. 2.124 $$RCOOR' + H_2O \longrightarrow RCOOH + R'OH$$

where R and R' can be any alkyl or acyl moiety. Although this equation accurately depicts the stoichiometry of ester hydrolysis, it does not serve as a defining equation for computing the velocity of the reaction. The rate of transformation of any specific ester is fundamentally dependent on its chemical structure. The speed of the reaction often depends on the pH of the medium as well, however, because ester hydrolysis can proceed via three distinct pathways (acid/base catalysis, neutral) with identical net stoichiometry.

Because chemical reactions involve shifts in electronic bonding orbitals, organic compounds are most readily attacked by groups that can donate or accept electrons from the target molecule. Electron-deficient chemical species (e.g., hydrogen ions) are called "electrophiles." Electrophiles are particularly attracted to atoms with negative charge, to a lone pair of electrons, and to the electron-dense region of a double bond. Chemical groups with extra non-bonding electrons are called "nucleophiles." The electronegative hydroxide ion is a relatively strong nucleophile. The water molecule is itself nucleophilic, because the oxygen atom of this "polar" molecule has a lone pair of electrons.

The mechanisms of the formation and hydrolysis of organic esters have been reviewed by Kirby (1972). Tinsley (1979:105 ff) has summarized the routes and mechanisms of ester hydrolysis under environmental conditions, where in all probability only the "A(AC)2" and "B(AC)2" mechanisms are significant. Although all three routes of ester hydroysis involve nucleophilic phenomena, the mechanism of the pathway is somewhat different in each case.

Acid-catalyzed ester hydrolysis is a true "catalysis" reaction in that hydronium ion participates in the reaction but is not consumed by the reaction sequence. In the first step of this pathway, the electrophilic hydronium ion protonates the carbonyl (C=O) oxygen. The protonated ester then undergoes a nucleophilic addition of water to give a tetrahedral intermediate; this step is catalyzed by a second water molecule acting as a general base. Finally, the tetrahedral intermediate breaks down via two additional (fast) steps to yield the product carboxylic acid and alcohol, and to regenerate the catalytic hydronium ion.

Because two water molecules are involved in the formation of the tetrahedral intermediate, the specific-acid catalyzed hydrolysis of the ester bond is "second-order" in water. With water as the solvent medium for the dissolved phase of the compound, however, the water concentration does not change during the course of the reaction and need not be incorporated in the kinetic expression. The observed rate constants are nonetheless subject to solvent effects and should be measured using pure water as the solvent whenever possible. The direct involvement of the water molecule in the reaction also imposes a need for care in the extrapolation of hydrolysis rate constants (measured in pure water) to compounds sorbed with sediments.

In EXAMS, all concentrations are referenced to the water phase of each compartment (Eq. 2.1). The total pollutant concentration C (units mg/liter of water), when multiplied by the appropriate distribution coefficient ALPHA, gives the dissolved concentration of pollutant in the aqueous phase of each compartment, including that in the interstitial pore water of a benthic sediment. This fraction of the pollutant hydrolyzes at the rate measured via a homogeneous phase (pure water) experiment. EXAMS computes the effects of residence in a sorbed state (where water concentration can be quite small) on the reactivity of the compound via an additional set of input parameters (Section 2.3.4.3).

Neutral hydrolysis of organic esters proceeds via a mechanism similar to that of the second stage of the acid-catalyzed pathway. Two molecules of water are again involved in the formation of a tetrahedral intermediate, with one molecule of water acting as the nucleophile and a second water acting as a general base catalyst. Although the neutral reaction is usually treated as a simple first-order process (Wolfe 1980), it is in fact technically second-order in water concentration. For this reason, the reaction is subject to solvent effects, and requires the same caution in extrapolation to sorbed states as was described above for acid-catalyzed hydrolysis.

Alkaline hydrolysis, the third hydrolytic mechanism considered in this Section, is not strictly speaking a hydroxide-"catalyzed" reaction, for hydroxide ion is consumed in the reaction sequence, yielding the ester's constituent alcohol and the anion of its carboxylic acid. At trace concentrations of the ester in buffered natural waters, however, this distinction is of no practical significance. As in the neutral and acid-catalyzed pathways, a tetrahedral intermediate species is probably involved in alkaline hydrolysis. In this case, however, the intermediate is usually envisioned as resulting from a direct nucleophilic attack of hydroxide ion on the carbonyl carbon, with formation of the tetrahedral intermediate as the rate-limiting step in the reaction pathway. The tetrahedral intermediate then breaks down via release of an R'O- anion, and rapid proton transfer (to R'O-), to yield the products of the reaction (R'OH and RCOO-).

The overall rate of hydrolytic transformation is thus the sum of three competing reactions, and the observed rate constant (Kobs, units /hr) can be computed as the sum of contributions from acid-catalyzed (KAH), neutral (KNH), and base-catalyzed (KBH) reactions (Wolfe 1980):

Eq. 2.125 $$Kobs = (KAH)[H+] + KNH + (KBH)[OH-]$$

Kobs is a pseudo-first-order (/hr) rate constant under the specified environmental conditions (pH, pOH) in pure water. After incorporation of the effects of ionization and sorption on reactivity, Kobs becomes the hydrolytic contribution to the overall pseudo-first-order rate constant K of Eq. 2.1. The second-order transformation rate constants are part of EXAMS' input chemical data base. KAH and KBH have units of reciprocal molarity and reciprocal hours (/M/hr). KNH, the neutral hydrolysis rate constant, has units /hr. The environmental data for this computation is entered as a separate pH and pOH for each sector (compartment) of the ecosystem; the EXAMS variables are "PHG" and "POHG," respectively.

The utility of this approach is not, of course, limited to chemical transformations of carboxylic acid esters. For example, amides, carbamates, and organophosphates break down via hydrolytic mechanisms (Tinsley 1979). Also, many halogenated compounds are subject to unimolecular and bimolecular nucleophilic substitution (SN1 and SN2) or elimination (E1 and E2) reactions whose kinetics can be represented via Eq. 2.125.

Experimental studies of the rate of hydrolysis in buffered aqueous solution can be used to determine Kobs at fixed pH levels. In many cases KAH and KBH can be determined at low and high pH, respectively, where only one reaction pathway is significant. The pH-rate profile, a plot of log Kobs vs. pH, then includes a descending (acid catalyzed) and ascending (alkaline) limb, with slopes of -1.0 and +1.0, respectively (Figure 2.6). These lines intersect at the theoretical rate minimum, giving the best pH for an experimental determination of any neutral contribution (KNH). One or more of the reaction pathways may be undetectably slow for a particular compound, resulting in a simplified pH-rate profile. (The use of pH-rate profiles for calculating hydrolysis rate constants has been described in more detail be Kirby (1972:153) and by Mabey and Mill (1978).)

Reported chemical rate constants are often based on the second or minute as the unit of time. For use in EXAMS, such data must be converted to units based on the hour. For example, the neutral hydrolysis rate constant of phenyl acetate is 6.6E-8 /sec (Figure 2.6). EXAMS' chemical input parameter (KNHG, units /hr) would be

6.6E-08 (/sec) * 3600 (sec/hr) = 2.38E-4 /hr.

2.3.4.1 Temperature effects

Each hydrolytic rate constant in EXAMS' chemical data base (KAHG, KNHG, KBHG) has a paired input parameter that allows for alternative entry of the chemical information as an (Arrhenius) function of temperature. The pairings are KAHG - EAHG, KNHG - ENHG, and KBHG - EBHG, respectively. The rate constant variables (KAHG etc.) are interpreted as the (Briggsian logarithm of the) "pre-exponential" or "frequency" factor in an Arrhenius function, only when the parallel activation energies (EAHG etc.) are non-zero. When the input energy parameter is set to zero, EXAMS accepts the kinetic parameter (KAHG, etc.) as the rate constant itself (compare Section 2.3.2.1). For example, an activation energy (Ea) for the neutral hydrolysis of phenyl acetate (ENHG) of, say, 20,000. cal/mole would imply a frequency factor A of:

A = KNH / exp(-Ea/RT)

(T in Kelvin) or, given KNH = 2.38E-4 /hr at 25 degrees C (Figure 2.6),

A = 2.38E-4 / exp(-20000./(1.99*298.15)) = 1.04E11 /hr

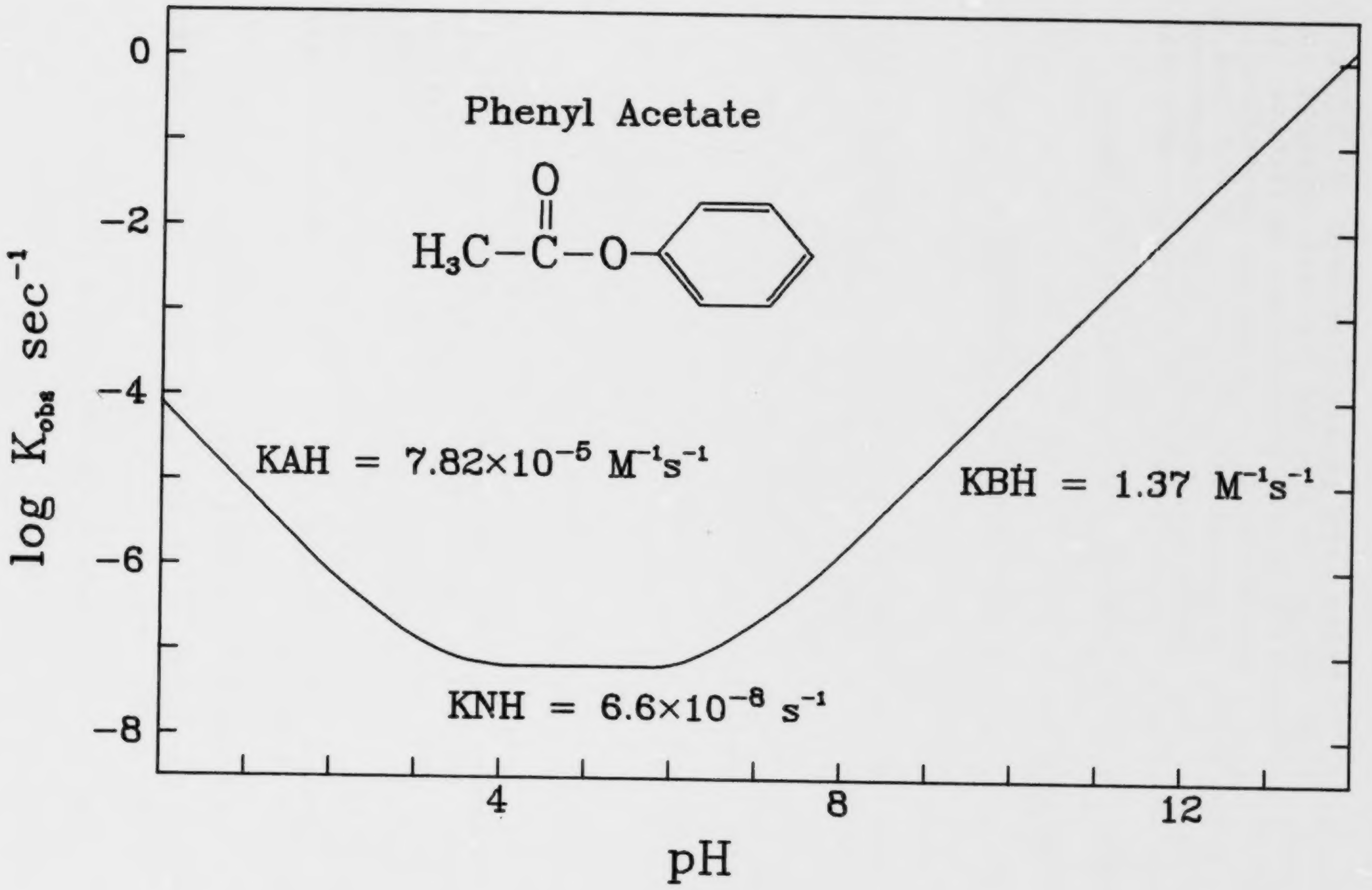

Figure 2.6. Hydrolysis pH–rate profile of phenyl acetate at 25 degrees C. Profile constructed via rate constant data summarized by Mabey and Mill 1978.

and log A, the EXAMS input (KNHG) would = 11.02 /hr.

In this instance, if EXAMS were loaded with KNHG = 2.38E-4 and ENHG = 0.0, KNHG would be used as the rate constant for neutral hydrolysis irrespective of the temperature (environmental input parameter TCELG) obtaining in the system compartments. Alternatively, EXAMS could be loaded with KNHG = 11.02 and ENHG = 20.0. In the latter case EXAMS would compute local (compartment specific) values of the neutral hydrolysis rate constant KNH via:

$$\log KNH = KNHG - ((1000.*ENHG) / 4.58 (TCELG + 273.15))$$

or, at TCELG = 25 degrees C,

$$\log KNH = 11.02 - (1000)(20)/(4.58)(298.15) = -3.626$$

and

$$KNH = 2.36E{-}4 \ /hr.$$

In many cases the temperature dependence of a chemical rate constant is reported in terms of transition state theory, that is, as an enthalpy (H) and entropy (S) of activation. Given H in calories/mole and S in cal/deg/mole (also called "entropy units," e.u.), data reported under this convention can be converted to Arrhenius functions via (Bunnett 1961):

Eq. 2.126 $Ea = H + RT$ (calories/mole)

and

Eq. 2.127 $\log A = S/4.58 + \log T + 14.319$ (/hr)

(Because the RT term is only about 600 cal/mol at room temperature, however, in many cases reported values of H are in fact uncorrected Arrhenius activation energies (Ea).) For example, Wolfe and coworkers (1977) found that malathion (O,O-dimethyl-S-(1,2-dicarbethoxy)ethylphosphorodithioate) breaks down via an acid catalyzed degradation with an enthalpy of activation (H) of 22.3 kcal/mol and an entropy of activation (S) of -4.1 eu. Using 15 degrees C as the temperature for conversion, Eq. 2.126 gives

$$Ea = 22300 + (1.987)(288.15) = 22872. \text{ cal/mol}$$

and an EXAMS input of EAHG = 22.87 kcal/mol. The frequency factor A (Eq. 2.127) would be:

$$\log A = -4.1/4.58 + \log(288.15) + 14.319$$

yielding log A = 15.88 /hr = KAHG.

When a compound is subject to more than one degradation pathway, the rate constants must be combined prior to entry in

EXAMS' chemical data base. For example, malathion undergoes an alkaline carboxyl ester hydrolysis plus an E2 elimination reaction kinetically dependent on hydroxide ion concentration [OH-] (Wolfe et al. 1977). These authors computed entropies and (uncorrected) enthalpies of activation for both reactions; this information could be used to generate an Arrhenius approximation for the total alkaline disappearance rate constant KBH via the transition state theory equation

Eq. 2.128   KHB (/hr) = (7.5018E13)(T) exp (-H/RT) exp (S/R)

where H = Ea - RT, as in Eq. 2.126. Whenever possible, however, it is probably better to rely on experimental determinations of the total disappearance rate constant, measured at environmentally relevant temperatures. In this case, the total (second-order) disappearance rate constant was measured at 0 and at 27 deg. C; it was 0.067 and 5.5 /M/s, respectively. The activation energy and frequency factor can be easily computed from this data, giving KBHG = 23.67 /hr and EBHG = 26.6 kcal/mole.

2.3.4.2 Ionization effects

Anions and cations of organic acids and bases can hydrolyze at rates differing greatly from those of the parent unionized species. This phenomenon can give rise to pH-rate profiles very unlike the archetypal example of phenyl acetate (Figure 2.6), including an apparent kinetic dependence on fractional powers of [H3O+] or [OH-]. In order to encompass these phenomena, each of EXAMS' input kinetic parameters (and parallel activation energies) was set up as a 3X5 matrix of variables. The second index of these parameter matrices specifies the ionic species for which a particular rate constant applies. (The first index allows for specification of the effects of sediment- and bio-sorption on reactivity; this aspect of EXAMS' input data is discussed in Section 2.3.4.3.)

Consider, for example, the hydrolysis of the series of substituted 2-phenyl-1,3-dioxanes studied by Bender and Silver (1963). All the acetals in the series showed the usual acid-catalyzed hydrolyses, but those members containing an o- or p-phenolic substituent were reactive at alkaline pH as well. The pH-rate profile for one member of this series, 2-(4-hydroxy-5-nitrophenyl)-1,3-dioxane ("HND"), is shown in Figure 2.7. This profile includes a descending limb of slope -1.0 at low pH, a zone of little change in Kobs suggestive of a neutral mechanism, followed by a second descending limb in the alkaline pH range, which begins in the vicinity of pH = pKa.

From a comparison of the kinetics of o- and p-phenolic substituted acetals, and from the effect of deuterium oxide on

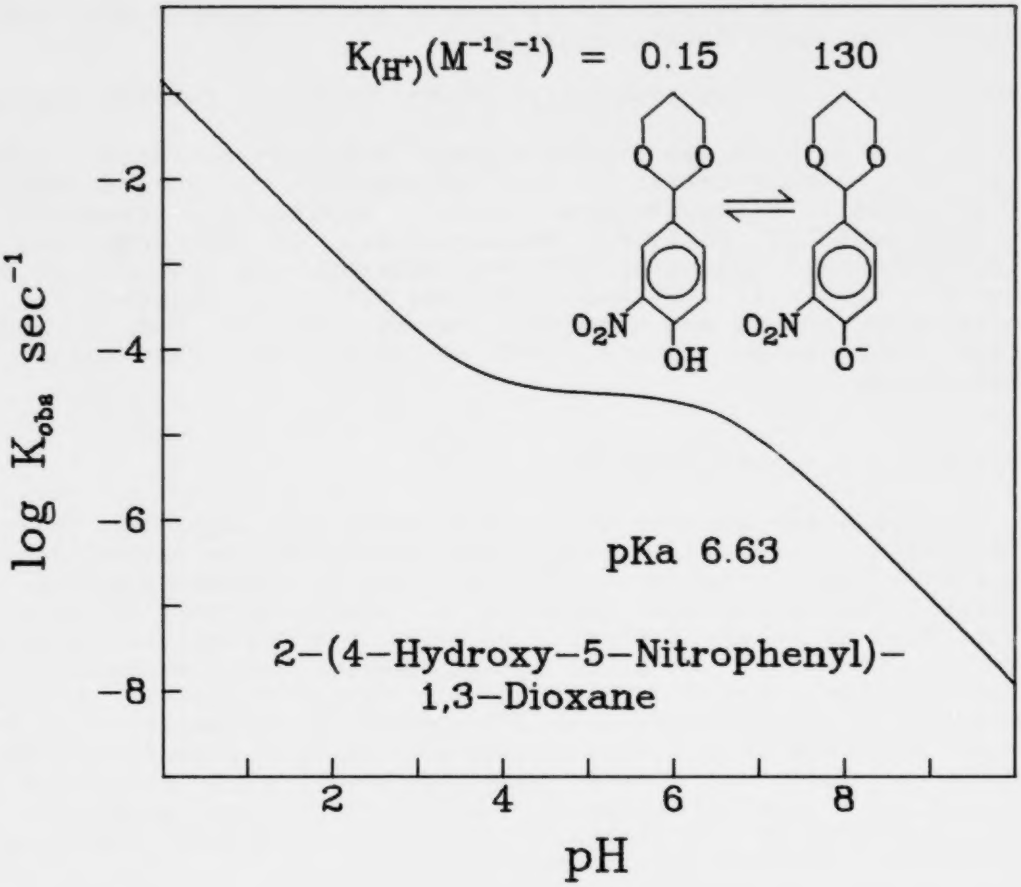

Figure 2.7. Hydrolysis pH–rate profile for a substituted 2–Phenyl–1,3–Dioxane. Data from Bender and Silver 1963.

these kinetics, Bender and Silver (1963) concluded that the hydrolysis of these compounds does not proceed via a neutral mechanism. Instead, the initial descending limb is the result of the usual acid-catalyzed hydrolysis of the unionized species, and the descending limb in the alkaline pH region results from a similar acid-catalyzed hydrolysis of the phenolate anion (Figure 2.7). The anion is 860 times more reactive than the unionized species. The uniformity of Kobs at intermediate pH results from the increasing importance of the phenolate anion, as a fraction of the total concentration, in this pH range.

The hydrolytic kinetics of HND can be completely specified in EXAMS' chemical data base via the pKa of the compound and the rate constants for acid hydrolysis (KAHG) of the uncharged and the anionic species. The existence of the unionized species and the phenolate anion is signalled by setting SPFLG(1) and SPFLG(4) to 1 (Section 2.2.1), and the pKa of HND is specified via PKAG(1) = 6.63. The second-order rate constants are 540. and 4.68E5 /M/hr for the parent compound and the anion respectively (Figure 2.7). This information is loaded to EXAMS by setting KAHG(1,1) to 540, and KAHG(1,4) to 4.68E5. The first index (Section 2.3.4.3) simply denotes the form of the compound (1 = dissolved). The second index specifies the ionic species to be transformed. Subscript (1,1) thus specifies the unionized dissolved HND as reacting at rate (540)[H3O+] /hr, and subscript (1,4) specifies the phenolate anion as reacting at rate (4.68E5)[H3O+] /hr.

2.3.4.3 Sorption effects

Sorption of a compound either with sediment phases or with living biomass removes the compound to a microenvironment that can be very different from the free water phase of the system. For example, Miller and Zepp (1979b) found that the daughter product yields resulting from photolysis of DDE shifted from p,p'-dichlorobenzophenone toward DDMU (1,1-bis(p-chlorophenyl)-2-chloroethylene) when the parent DDE was sorbed with suspended sediments. Photolysis of DDE dissolved in hexane also gave enhanced yields of DDMU. The authors concluded that the sorbed compound experienced a microenvironment similar to that of an organic solvent, and very different from that of the aqueous phase.

Similar effects can be postulated for the majority of modes of chemical reaction of organic compounds in the environment. Presumably reactions like the neutral hydrolysis of carboxylic acid esters, in which the water molecule participates in the reaction, would be substantially inhibited by residence of the target molecule in a sorbed state. An E1 or SN1 reaction might be little affected, however. Furthermore, the possibility of accelerated (sediment "catalyzed") reactions cannot be disregarded. Although no definitive studies on the effects of residence in a sorbed state on chemical reactivity have appeared in the literature, such exploratory experiments as have been undertaken indicate that sorption "protects" many compounds from hydrolytic transformation. This is not a universal phenomenon, however, for in some cases the reactivity of compounds was not affected by residence in a sorbed state (Wolfe 1980 (in prep.)).

Obviously, then, the differences between the sorbed form of an organic compound and its dissolved phase can be as profound as the differences between, for example, an organic acid and its anions (Section 2.3.4.2). EXAMS therefore provides for the entry of rate constants (or Arrhenius functions) that specify the kinetics of sorbed forms completely independently of the reactivity of the aqueous dissolved phase of the compound. Each named kinetic parameter is a matrix with 15 elements, allowing for up to 5 ionic species with 3 forms (dissolved, sediment-sorbed, and biosorbed) of the parent (uncharged) compound and of its ions.

EXAMS computes the rate of reaction of the sorbed species under the assumption that the reaction is first-order in sorbed substrate. The model used to calculate these reaction rates can be described via a simplified example. In general, the rate of transformation of dissolved compound is given by:

Eq. 2.129 $d(Cw)/dt = - Kw\ Cw$

where Cw is aqueous concentration (mg/L) and Kw is a first-order (or pseudo-first-order) rate constant (units /hr). Similarly, the rate of transformation of the sorbed phase of the compound can be taken as:

Eq. 2.130 $d(Cs)/dt = - Ks\ Cs$

where Cs is the concentration of the sorbed phase of the compound (mg/kg dry sediment) and Ks is a first-order rate constant.

Under EXAMS' assumption that a rapid (i.e., faster than the reaction rates) sorption equilibrium is maintained, Cw and Cs are in constant proportion to Ct, where Ct is the total concentration of pollutant in the system. (In this context, "system" is equivalent to a single ecosystem sector (compartment), a well-mixed chemical apparatus, etc.) Within EXAMS, chemical concentrations are carried internally in units of mass/unit aqueous volume. Consequently the total rate of transformation of a compound is represented as:

Eq. 2.131 $d(Ct)/dt = Kw\ Cw + R\ Ks\ Cs$

where R is the sediment/water ratio (kg/l), that is, SEDCOL in the language of Section 2.2.2.

Given that the assumption of a rapid local sorption equilibrium holds good, however,

Eq. 2.132 $C_w = ALPHA(1)\ C_t$, and

Eq. 2.133 $R\ C_s = ALPHA(2)\ C_t$, where

Eq. 2.134 $ALPHA(1) = 1/(1 + (K_p)(R))$, and

Eq. 2.135 $ALPHA(2) = (K_p*R)/(1 + (K_p)(R))$

(Kp the partition coefficient), as described in Section 2.2.4. Substitution of Eq. 2.132 and Eq. 2.133 into Eq. 2.131 gives:

Eq. 2.136 $d(C_t)/dt = (\ ALPHA(1)(K_w) + ALPHA(2)(K_s)\ )\ C_t$

Equation 2.136 is (a simplified form of) the defining equation used to build EXAMS' algorithm for combining the reactivity of dissolved and sorbed forms into a single pseudo-first-order rate constant.

The simplicity of this model makes the conversion of experimental observations into a form suitable for EXAMS relatively straightforward. Suppose, for example, that a neutral organic compound ("NOC"), subject to a pH-independent transformation, is observed to have a half-life in pure water of 33 hours. The rate constant describing this process is:

$$K_w = -(\ln 0.5)/33 = 0.021\ /hr$$

This rate constant enters EXAMS' chemical data base via KNHG(1,1) = 0.021. The first subscript of KNHG denotes the dissolved form (1) of the compound; the second denotes an uncharged molecule. (As NOC is a neutral compound, only SPFLG(1) is set (i.e., = 1), and SPFLG(2), (3), (4), and (5) are 0, denoting the non-existence of any ionic species.)

Suppose, now, that NOC has a partition coefficient on a particular sediment of 90000 (mg/kg)/(mg/L), and an experimental determination is made of the half-life of the compound after sorption equilibration on a 100 mg/L suspension of the sediment. (So long as local sorption equilibrium is maintained, the half-life can be ascertained by following either Cw or Cs over time.) The fraction of Ct present as dissolved and as sorbed NOC can be computed via Eqs. 2.134 and 2.135. The sediment/water ratio R is (100 mg/L) * (1.E-6 kg/ml) = 1.E-4 kg/L; the dissolved fraction is:

Eq. 2.137 $ALPHA(1) = 1\ /\ (1+(90000)(1.E-4)\ ) = 0.10$

and the fraction sorbed is:

Eq. 2.138 $ALPHA(2) = (90000)(1.E-4) / (1+(90000)(1.E-4)) = 0.90$

This experiment has three obvious possible outcomes. First, sorption may have no effect on the reactivity of the compound. Second, the observed half-life may be increased in strict proportion with ALPHA(1), that is, sorption may "protect" the compound. Finally, an altered half-life may be indicative of an altered, but non-zero, reactivity of the sorbed phase of the compound.

In the first case, when the presence of the sediment suspension has no effect on the rate of transformation of the compound, Ks is identically the same as Kw. EXAMS could then be loaded with KNHG(2,1) = 0.021. The subscript "2" denotes the sediment-sorbed form of NOC.

When residence in a sorbed state inhibits the transformation reaction, the observed rate constant Kobs will decrease in proportion with the residual water concentration of the compound. From Eq. 2.136,

$$Kobs = ALPHA(1)*Kw + ALPHA(2)*Ks$$

In this example, ALPHA(1) = 0.10, and, if Ks = 0 then

$$Kobs = (0.10)(0.021) = 0.0021 \text{ /hr.}$$

The possibility that sorption "protects" the compound can thus be evaluated via the compound's half-life in a sediment suspension. Here, given Kobs = 0.0021, the half-life Tau is given by:

$$Tau = -(\ln 0.5)/(0.0021) = 330 \text{ hours.}$$

In other words, an observed half-life that was not significantly different from 330 hours would be a clear indication that Ks = 0, and EXAMS could be loaded with KNHG(2,1) = 0.

Finally, the observed half-life may be neither 33 nor 330 hours, indicating that the sorbed state, while reactive, does not transform at the same rate as the aguueous-phase dissolved compound. (In the event that the observed half-life were longer than 330 hours, Ks would be negative. The most probable explanation of such an event, however, is that either the sediment was contaminated with the study compound prior to the experiment, or that the assumption of rapid local equilibrium has been violated.) Any half-life between 0(+) and 330 hours can be converted to a value of Ks via Eq. 2.136. If the half-life were less than 33 hours, the transformation must have been accelerated in the sediment phase and Ks > Kw. Suppose, however, that the half-life of NOC in the 100 mg/L sediment suspension was 150 hours. The first-order rate constant Kobs is then:

$$Kobs = -(\ln 0.5)/(150.) = 4.621E-3.$$

Given $$Kobs = ALPHA(1)\ Kw + ALPHA(2)\ Ks,$$ then

$$4.621E-3 = (0.1)(0.021) + (0.9)\ Ks$$

and Ks = 2.80E-3. The rate of reaction of NOC in the sorbed state was thus 13.3% of that of the dissolved phase of the compound. This information could now be entered into EXAMS via KNHG(2,1) = 2.8E-3.

Second-order pH-mediated reactions ocurring on sediments are accommodated in EXAMS in a wholly analogous way. EXAMS uses the solution-phase pH and pOH to compute rates of reaction, so of course the input data must also be developed from this perspective. The full 15-element matrices of KAHG, KNHG, and KBHG allow for the specification of effects of both sediment- and bio-sorption on first-order, [H3O+] mediated, and [OH-] mediated reactions. In addition, any of these rate parameters can alternatively be specified via an Arrhenius function, as described in Section 2.3.4.1.

2.3.5 Oxidation

Direct photolysis is not the sole pollutant transformation process driven by the solar flux in aquatic systems. The simultaneous occurrence of plant decomposition products ("humic materials"), dissolved oxygen, and sunlight often results in an acceleration of the rate of transformation of organic pollutants. Zepp and coworkers (1977), for example, found that methoxychlor, with a direct photolysis halflife of more than 300 hours, had a halflife of as little as 2.2 hours under irradiation in natural waters containing dissolved humic materials. Further, Ross and Crosby (1975) found that a solution of aldrin in water from a taro paddy can be photochemically converted to dieldrin, despite the fact that aldrin does not absorb sunlight.

These kinds of reactions are usually termed "indirect" or "sensitized" photolysis. Indirect photolysis can be subdivided into two general classes of reactions. First, "sensitized photolysis" per se involves sunlight absorption and electronic excitation of a sensitizer (humic) molecule, followed by direct chemical interaction between the excited state of the sensitizer and a pollutant molecule. Possible chemical reactions include a direct energy transfer to the pollutant molecule, hydrogen atom transfer from pollutant to sensitizer to give free radicals, and union of sensitizer and pollutant yielding an excited-state complex or "exciplex" (Zepp and Baughman 1978). The resulting free radicals or exciplexes can then react with dissolved molecular oxygen, a process termed "type I sensitized photooxidation" by these authors.

The second class of indirect photolysis involves the formation of chemical oxidants in natural waters, primarily via the interaction of sunlight, humic materials, and dissolved oxygen (type II sensitized photooxidation of Zepp and Baughman 1978). The primary oxidants known to occur in natural waters are hydroxyl and peroxy radicals (Mill, Hendry, and Richardson 1980), and singlet oxygen (Zepp et al. 1977). Alkoxy radicals and diradicals may also contribute to environmental oxidation of some compounds, but their presence in natural waters has not been conclusively demonstrated (Mill 1980).

EXAMS represents the oxidative transformation of pollutants via a purely phenomenological coupling of a second-order rate constant (KOXG, units /M/hr) to user entries for the molar concentration (OXRADG, moles/liter) of oxidants in each ecosystem compartment. The pseudo-first-order contribution of oxidation processes to the overall transformation rate constant K of Eq. 2.1 is computed for each (I) compartment via:

Eq. 2.139 $$K\ (/hr) = KOXG * OXRADG(I)$$

The input parameter KOXG is again a 3X5 matrix, allowing for separate entry of rate constants of ionic species and for control of the effects of sorption on reactivity. The subscripts have the same significance and use as described for KAHG etc. in Section 2.3.4. Effects of temperature are entered via a parallel matrix of Arrhenius activation energies EOXG (kcal/mole), again as described in Section 2.3.4 for hydrolytic reactions.

The occurrence and concentration of oxidants in natural waters has been investigated via the irradiation of chemical "probes" in a laboratory setting. Zepp and coworkers (1977) studied the generation of singlet oxygen using solutions of 2,5-dimethylfuran (DMFN) in natural waters. DMFN gives 1,2-diacetylethylenes via 1,4-addition of singlet oxygen. The speed of this reaction upon irradiation of the solution gives a quantitative measure of the steady-state concentration of singlet oxygen in the solution. Similarly, Mill and coworkers (1978, 1980) have used cumene (isopropylbenzene) and pyridine as chemical probes for the steady-state concentrations of peroxy and hydroxyl radicals in irradiated natural waters.

Some results of these studies are given in Table 2.24. The average steady-state molar concentrations of oxidants were on the order of 1.E-13 for singlet oxygen, 1.E-9 for peroxy radicals, and 1.E-17 for hydroxyl radicals.

Table 2.24. Steady-state concentrations (moles/liter) of oxidants in some natural waters*

Source	Singlet Oxygen	Peroxy Radical	Hydroxyl Radical
	X 10^{13} M	X 10^{9} M	X 10^{17} M
Aucilla River, FL	18.	2.8	1.8
Okefenokee Swamp, GA	22.		
Mississippi River, LA	5.		
Coyote Creek, CA		9.1 5.0	1.6
Boronda Lake, CA		9.5 0.45	0.15

* Data from Mill, Hendry, and Richardson 1980; Zepp et al. 1977

These concentrations were determined via photolysis of thin layers of solution, and are presumably dependent on the intensity and spectral distribution of the solar flux in the solution. Because light extinction in the water column reduces the volumetric average solar flux below that at the air-water interface, the oxidant concentrations given in Table 2.24 apply only to the surface zone of natural bodies of water. The effect of light extinction can be computed from the equation:

Eq. 2.140 $$I/Io = (1 - \exp(-kZ)) / kZ$$

where I/Io is the average light intensity as a fraction of its surface value (Io), k is a diffuse attenuation coefficient (/m), and Z is the depth of the compartment (m). The factor I/Io can be used to generate depth-corrected oxidant concentrations for use in EXAMS. Alternatively, the program itself can be used to generate correction factors, using the input variables and program outputs described in Section 2.3.3.

EXAMS allows for the entry of environmental concentrations of only one kind of oxidant. For a compound reactive with more than one oxidant species, the rate constant and environmental concentration giving the most significant transformation rate can be entered, or a composite rate constant and environmental oxidant concentration can be computed and loaded in the data bases.

Although the mechanism of generation of oxidants of course precludes their occurrence in benthic sediments, EXAMS does not preclude the entry of a non-zero value of OXRADG for a "B"-type compartment. If OXRADG for a benthic compartment is non-zero, EXAMS simply computes a reaction rate via coupling to KOXG, and adds the result to the overall pseudo-first-order transformation rate constant (K in Eq. 2.1). This feature allows OXRADG and KOXG to be used as "free parameters" for evaluation of processes not explicitly respresented in EXAMS. For example, Mulkey and Burns (1980), in a simulation study of the effects of small reservoirs on pollutant dynamics, loaded data describing reductive dechlorination of toxaphene into EXAMS. This was accomplished by setting OXRADG to 1.0 for benthic compartments and to 0.0 for all water column compartments, and then using the KOXG matrix to load pseudo-first-order rate constants for reductive dechlorination of the compound in bottom sediment zones.

2.3.6 Microbial Transformations

Microbial communities are a ubiquitous constitutent of almost all aquatic ecosystems. The microbiota play a central role in the remineralization of plant and animal debris; they have evolved the capacity to transform and harvest energy from an immense array of naturally occurring organic compounds. The optimistic hope that "the solution to pollution is dilution" to some extent had its origin in a naive faith in the ability of saprobic microbes to utilize any and all synthetic organic compounds in their metabolic mills.

Total faith in the ability of natural systems to absorb and detoxify synthetic chemicals was, of course, shaken by the discovery of the world-wide dispersal (and bioconcentration) of synthetic biocides, notably DDT and the related compounds DDE and DDD. It is now "axiomatic that micro-organisms are fallible and that many synthetic organic compounds are recalcitrant ... and accumulating in some environments" (Alexander 1979a). In consequence, qualitative "biodegradability" tests (Swisher 1970) are now routine in the detergent industry, and "sludge" tests have been suggested (Buzzell, Thompson, and Ryckman 1969) as a routine procedure for evaluating industrial synthetic organic compounds. The latter tests can also provide some assurance that the compound will not destroy the microbial communities that serve man in sewage treatment plants, as well as providing an evaluation of the biodegradability of the compound (e.g., Baird et al. 1974).

The discovery of microbial fallibility has led to a more critical and quantitative view of microbial metabolism of synthetic organics; it no longer suffices to know that a compound is "biodegradable." Instead the rates, products, microbial populations, and environmental conditions surrounding an observed biodegradation are of increasing interest to the microbiological and ecological community. Given that the natural microbial substrates can massively accumulate in special circumstances (e.g., peat bogs and swamps), a degree of skepticism is obviously warranted toward any claim of universal, unconditional biodegradability of a synthetic organic compound. The rates at which a compound is biodegraded must depend upon both the structure of the compound, and on the metabolic capacity of the microbial community resident in the ecosystem receiving the compound.

Microbial communities derive energy for metabolism and growth from the breakdown of organic compounds, and the kinetics of growth and substrate utilization have been of interest to microbiologists for many years. Both population growth and substrate utilization rate have been described via Monod's (1943) analogy with Michaelis-Menten enzyme kinetics (Slater 1979). In this approach, the growth of a microbial population in an unlimiting environment is described by:

Eq. 2.141 $$dN/dt = u\ N$$

where u is called the "specific growth rate" and N is microbial biomass or population size. The Monod equation modifies Eq. 2.141 via the recognition that consumption of resources in a finite environment must at some point curtail the rate of increase (dN/dt) of the population. This fact was incorporated into Eq. 2.141 via:

Eq. 2.142 $$u = u(\max) \frac{[S]}{Ks + [S]}$$

in which [S] is the concentration of the growth limiting substrate, u(max) is the "maximum specific growth rate" obtaining when [S] is present in excess (i.e., non-limiting), and Ks, the "saturation constant" is that value of [S] allowing the population to grow at rate u(max)/2. An equation describing the behavior of the growth substrate [S] over time, and thus by implication the dynamics of a biodegradable synthetic compound, follows via a simple derivation (Slater 1979): Assuming that a fixed amount of growth results from metabolism (and therefore loss from solution) of a unit quantity of S, then

Eq. 2.143 $$dN = -Y\ dS$$

where Y is the "yield coefficient" in cells or biomass produced per unit S metabolized. Taking

Eq. 2.144 $$\frac{dS}{dt} = \frac{dS}{dN}\frac{dN}{dt}$$

gives

Eq. 2.145 $$dS/dt = -(u/Y)\ N$$

or, substituting Eq. 2.142 for u,

Eq. 2.146 $$\frac{dS}{dt} = -\frac{u(max)}{Y}\frac{[S]}{Ks + [S]}\ N$$

The observed microbial growth yield Y is often calculated from the amount of microbial biomass produced during the course of transformation of a measured quantity of substrate. Because a microbial population must satisfy maintenance requirements before any growth can occur, the apparent yield Y can fall quite drastically at low concentrations of S. Expressions with separated growth and maintenance yields have been developed by Pirt (1975), and it is possible to compute the separate magnitudes of growth and maintenance yields from microbial growth experiments (Slater 1979).

The Monod formulation (Eq. 2.146) has been successfully applied to biotransformation of synthetic chemicals in a laboratory setting. These studies have demonstrated that a Monod analysis need not be restricted to single-species populations, that is, the Monod equations can serve as adequate descriptors of substrate transformation by "mixed" or "heterogeneous" (i.e., multi-species) microbial populations. In one example, Paris, Lewis, and Wolfe (1975) isolated a 4-species consortium of organisms able to use malathion as its sole source of carbon. Analysis of the growth response of the population and of concurrent malathion transformation rates then gave the Monod parameters u(max) = 0.37 /hr, Ks = 2.17 uM/L (0.716 mg/L), and Y = 4.1E10 cells/uM (1.2E11 cells/mg). In a similar study, Smith and coworkers (1978) investigated the degradation of p-cresol by mixed microbial cultures able to use the compound as a sole carbon source. These authors expressed their results in terms of Monod parameters, finding u(max) = 0.62 /hr, Y = 1.8E9 cells/mg, and Ks = 0.84 mg/L.

Unfortunately, these elegant applications of classical microbiological methods to the biotransformation or "biolysis" of synthetic organic compounds are difficult to apply in a broader ecological context. The first difficulty, which has received some attention in the microbiological literature, is primarily mechanical: The Monod formulation (Eq. 2.146) is non-linear in its parameters, and thus imposes a high cost in computation time when used in a computer program or mathematical model. For trace concentrations of pollutants (i.e., [S] << Ks), however, the term (Ks + [S]) in the denominator of Eq. 2.146 can be approximated by Ks, giving the linear approximation:

Eq. 2.147 $$\frac{d[S]}{dt} = -\frac{u(max)}{Y\ Ks} N\ [S]$$

This formulation is similar to the "second-order" equations used to describe the kinetics of chemical reactions, and the term u(max)/(Y Ks) can by analogy be termed a second-order biolysis rate constant Kb2, with units /hr/(cells/l) when population sizes N are expressed in cells/l.

The propriety of this substitution can be readily evaluated. For malathion, u(max)/(Y Ks) = 0.37/(4.1E10*2.17) =4.16E-12 /hr/(cells/l). Paris et al. (1975) also computed values of Kb2 from microbial population sizes and malathion transformation rates in their experimental studies, finding a mean value for Kb2 of (2.6+0.7)E-12 (95% confidence interval) /hr/(cells/l) for a series of 8 experimental determinations spanning a concentration range from 0.0273 to 0.33 uM in malathion. The measured Kb2 differed from u(max)/(Y Ks) by less than a factor of 2, suggesting that simplified kinetic experiments could be used to develop second-order rate constants, in lieu of a detailed elaboration of u(max), Y, and Ks, when the region of concern is restricted to levels of compound << Ks.

Furthermore, dissolved pesticide concentrations in surface waters are often very low indeed. For example, dieldrin, lindane, and DDT have been found primarily at ng/L levels both in the USA (Matsumura 1972) and in Britain (Brooks 1972). For industrial chemicals, however, the situation can be somewhat different. For example, the release of phenolic wastes into the St. Lawrence River results in riverine concentrations of 0.01 to 0.15 mg/L (Visser et al. 1977). Although these high concentrations are restricted to a dispersion cone immediately downstream of the effluents, Ks for p-cresol (0.84 mg/L) is uncomfortably close to the highest measured concentrations.

The need for a thorough evaluation of the propriety of Eq. 2.147 as an adequate approximation to the Monod formula (Eq. 2.146) disappears, however, upon examination of the conceptual difficulties standing in the way of the application of either equation to environmental situations. A natural microbial community derives its energy from a large variety of organic detrital materials. A microbial species restricted to a trace-level synthetic compound as its sole carbon source would be at a severe competetive disadvantage; there is no way of predicting a priori the population densities the degrader could attain in real systems. Even when a synthetic compound is sufficiently similar to natural substrates that it can be indifferently degraded by the microbial community as a whole, the presence of multiple energy-yielding substrates in the environment violates a fundamental assumption underlying the Monod approach, that is, that [S], the synthetic compound, limits growth. In many instances, moreover, a compound may be transformed or degraded in an energy-requiring detoxification process, making the concept of cell yield (Y) of dubious utility. When the compound, for whatever reason, is degraded in the absence of a change in population size, the apparent zero yield forces abandonment of Eq. 2.146 and 2.147 alike. (This phenomenon is sometimes called "cometabolism," e.g., Alexander 1979b; Jacobson, O'Mara, and Alexander 1980.)

Despite these difficulties, the rate of transformation of organic pollutants must depend on the structure of the compound and the metabolic capacity of microbial communities. The simplest expression of this duality is the second-order equation:

Eq. 2.148 $$d[S]/dt = - Kb2\ B\ [S]$$

which asserts that the rate of biolysis (d[S]/dt) is first-order in compound concentration [S] and in microbial activity B, and in which the identification of Kb2 with u(max)/(Y Ks) is discarded. This approach requires that the second-order rate constant be determined via laboratory studies of relatively undisturbed samples drawn from natural microbial communities. It also requires demonstration that d[S]/dt is linearly proportional to [S] for fixed levels of B, and that appropriate measures of B be found.

One conventional microbiological technique for characterizing microbial populations is simple population size, measured, for example, by colony counts on pour-plate agars (APHA 1976). To the extent that population size is an adequate measure of community metabolic capacity, simple microbiological techniques could serve to characterize the rate of biotransformation of synthetic compounds in natural environments. This hypothesis has been explored for three compounds (butoxyethyl ester of 2,4-D (2,4-DBE), malathion, and chlorpropham) by Paris and coworkers (Baughman, Paris, and Steen 1980; Paris et al. 1981). These authors investigated biotransformation of their study compounds in samples of natural waters drawn from 40 locations in the continental USA. Ambient water temperatures at the collection points ranged from 1 to 29 degrees C, and the laboratory studies were conducted at the observed ambient temperature of the sampled environments. Ambient bacterial populations, as measured by 48-hour incubation on TGE (tryptone glucose extract) agar at 22 degrees C, ranged from 4.E2 to 9.E5 cells/ml (Paris et al. 1981). Biolysis of these chemicals was demonstrably first-order in compound concentration and in population size, and was relatively independent of temperature. The 95% confidence intervals (based on between-site variation) for Kb2 (/hr/(cell/L)) and number of sites for these compounds were (5.42+0.97)E-10 (2,4-DBE, 31 sites), (4.54+0.74)E-11 (malathion, 14 sites), and (2.63+0.72)E-14 (chlorpropham, 11 sites).

Evaluation of biolysis in such "river die-away" studies is particularly difficult when a combination of small populations and slow rates of biodegradation leads to inconveniently long biolysis halflives. In such cases population densities must be augmented via centrifugation or supplemental nutrient broth. The latter procedure can have the disadvantage of favoring opportunistic heterotrophs at the expense of organisms better equipped to degrade more recalcitrant compounds. For example, the second-order biolysis rate constant (Kb2) for chlorpropham is unaffected when population densities are augmented via nutrient broth supplementation, but the measured Kb2 for phenanthrene decreases in approximate proportion with the the population increase (Paris, oral comm.).

Baughman, Paris, and Steen (1980) also reported second-order rate constants for biotransformation of synthetic chemicals by populations derived from aquatic sediments. The observed rate constants for 2,4-DBE and malathion were consistent with the rate of degradation by water-column populations, at Kb2 of 2.3E-10 and 4.0E-11 /hr/(cell/L) respectively. Aerobic biolysis of chlorpropham by the sediment-derived populations was almost an order of magnitude faster (Kb2 = 1.42E-13) than biolysis by the water-column populations (Kb2 = 2.4E-14 /hr/(cell/L)). By varying the sediment/water ratio, these authors also demonstrated that chlorpropham, methoxychlor, and several phthalate esters were unavailable to biolytic organisms when sorbed to suspended sediments.

Plate-count estimates of bacterial population densities are extremely selective and can underestimate total populations sizes by 3 or more orders of magnitude (Wetzel 1975:571, Fletcher 1979, Jannasch and Jones 1959). Furthermore, although increases in pollutant flux (that is, mg/L/time or mass degraded/time) with increasing chemical concentration (consonant with pseudo-first-order kinetics) have been observed in nature (e.g., Sherrill and Sayler 1980), it is also true that, at elevated pollutant concentrations, both a reduction in the apparent first-order rate constant (Tinsley 1979:149ff), and zero-order kinetics (Visser et al. 1977) have been observed. The latter phenomena are consonant (mathematically) with Eq. 2.146. It is not clear, however, whether these kinetics are a reflection of the maximum growth rate of a specialized sub-population of degraders or result from toxic effects of elevated concentrations on the microbial community.

In any case, it is clear that the studies of second-order kinetics cited above are a useful beginning in the detailed quantitative study of rates of biotransformation of pollutant chemicals. Little more extrapolative power can be developed until such time as the environmental coupling variables that govern the metabolic capacity of natural and laboratory microbial populations have been rigorously determined and measured in both kinds of systems.

As a first appoximation, EXAMS utilizes a simple second-order equation (Eq. 2.148) to compute the rate of biotransformation of pollutant chemicals. Microbial population densities for each sector of the ecosystem enter EXAMS' environmental data base via the BACTOG vector. For water column compartments, BACTOG has units of cells/ml; BACTOG for benthic compartments has units cells/100 g dry weight of sediment. (A useful summary of observed bacterial population densities in aquatic systems can be found in Wetzel 1975: 571-596.) Second-order biolysis rate constants enter EXAMS' chemical data base via separated parameters for water-column (KBACWG) and benthic (KBACSG) populations. The nominal units are /hr/(cell/ml) in both cases. EXAMS internally converts benthic microbial population densities to units (cells/ml of water) commensurate with the units of the rate constants KBACSG. This conversion is executed via the expression:

(BACTOG * SEDMSL)/(100. * WATVOL)

where SEDMSL is the mass of sediment in the compartment (kg), WATVOL is the volume of water contained in the compartment (liters) (Eq. 2.12 et seq.), and the numerical factor (100) is a units conversion term (1000 (ml/L) / 10 (decagrams (cwt)/kg). Finally, EXAMS also includes a dimensionless environmental parameter (ACBACG, nominal range 0.0 - 1.0) that can be used to specify the proportion of the total population that actively degrades the compound. This parameter can be used to modify rate constants developed from sole-carbon-source studies via an estimate of the representation of the degrader species in the microbial subsystem of each sector of the ecosystem.

Despite the ruthless parsimony imposed on EXAMS' representation of biolysis kinetics, the degree of chemical detail provided by EXAMS' allowance for ionic and sorptive speciation leads to fairly substantial opportunities for the inclusion of biolytic kinetic detail. Both KBACWG and KBACSG are 3X5 element matrices; each element represents a separate rate constant for the ionic and sorbed species of the pollutant. (The use of the matrix indices to specify chemical species is described in Section 2.3.4.) In addition, biolysis rate constants can be entered either as temperature-independent single values, or as functions of environmental temperatures. The effective average environmental temperature governing a biolysis rate (environmental input parameter BIOTMG) is separated from the temperature variable governing chemical reactions (TCELG), because a Q-10 function (rather than an Arrhenius function) is used to depict the effects of temperature on biolysis rates.

The Q-10s (i.e., increase in biolysis rate per 10 degree C change in temperature) for KBACWG and KBACSG occur as the parallel matrices QTBAWG and QTBASG, respectively. When the value of parameter QTBAWG or QTBASG is non-zero, EXAMS takes the corresponding member of KBACWG or KBACSG as the biolysis rate constant at 20 degrees C, and recomputes the second-order rate constant via the Q-10 equation:

Eq. 2.149
$$KBAC \longleftarrow KBAC_{(20)} * QTBA^{(BIOTMG - 20)/10}$$

The (compartment-specific) environmental temperature variable (BIOTMG) used in this computation has units of Celsius degrees; it is separated from the temperature variable (TCELG) used for chemical reactions in order that, if desired, Q-10 weighted averaging can be used to summarize observed environmental data. Because microbial communities frequently adapt their metabolic capacity to keep pace with slow secular (e.g. seasonal) changes in environmental temperatures, temperature responses measured in a laboratory setting do not always apply to environmental conditions. This limitation should be recognized when interpreting the results of EXAMS simulations that include temperature effects on biolysis rate constants.

Although the nominal units of BACTOG and KBAC include bacterial population densities expressed as numbers/ml, clearly these variables can in both instances be redefined to encompass any environmental coupling variable of utility in estimating biodegradation rates in aquatic ecosystems. It is, however, especially important that these units be commensurate: For example, if the rate constants were determined via viable plate counts, and the natural population estimated via direct counts, biolysis rates would probably be grossly overstated. Furthermore, the simple second-order equation allows for a multiplicity of estimators of microbial capacity. For example, Neely (1980: 117ff) lists 7 commonly used estimators of microbial biomass or activity, including counting techniques, ATP and DNA analyses, and oxygen uptake. By suitable (user) redefinition of the nominal units of KBAC and BACTOG, EXAMS can be used to compute pseudo-first-order rate constants as a function of environmental variation in the presumed governing variable, so long as KBAC and BACTOG are entered into EXAMS' data bases in commensurate units.

The mechanics of EXAMS' conversion of second-order biolysis rate constants and the compartment-specific environmental coupling variables to pseudo-first-order form are completely homologous with the equations used for chemical reactions. The total pseudo-first-order biolysis rate constant is accumulated as the sum of expressions of the form:

Eq. 2.150 Kb = ALPHA * KBAC * BACTO * ACBAC

where ALPHA is the fraction of the total pollutant concentration present in each existing ionic or sorbed chemical species, KBAC is the appropriate element of matrix KBACW or KBACS (corrected as needed for environmental temperatures), and (BACTO * ACBAC) is the degrader population density or metabolic capacity of the microbial community in each ecosystem compartment. The sum of these pseudo-first-order (/hr) expressions then becomes the biolysis contribution to the overall (compartment-specific) pseudo-first-order rate constant K of Eq. 2.1.

2.4 Input Pollutant Loadings

The flux of a pollutant chemical entering an ecosystem (term "Le" in Eq. 2.1) is a primary determinant of the ultimate exposure experienced by resident organisms. EXAMS does not compute pollutant loadings. Loadings may be developed via projected or measured industrial effluent fluxes, agricultural runoff, landfill seepages, etc., but these computations must be executed externally to EXAMS.

EXAMS provides input vectors for 5 kinds of loadings to each compartment of the system. These are: point-source or stream-borne loadings (STRLDG), non-point-source loadings (NPSLDG), contaminated ground-water seepage entering the system (IFLLDG), precipitation washout from the atmosphere (PCPLDG), and spray-drift (or miscellaneous) loadings (DRFLDG). The loadings have units of kg (of chemical)/hour in all cases. These loadings are taken as time-invariant constants in EXAMS' steady-state computations. Generally, therefore, the input loads should be developed (at least nominally) as long-term average values, although EXAMS can be adapted (at the user's discretion) to evaluate, for example, the consequences of shorter-term heavy loadings of kinetically labile compounds.

Each non-zero pollutant loading must conform to the hydrologic definition of the ecosystem, or EXAMS will not implement the loading. Thus EXAMS will cancel a STRLDG, NPSLDG, or IFLLDG for a given compartment, if that compartment does not receive an appropriate carrier flow STFLOG, NPSFLG, or INTFLG respectively. (Definition and entry of the hydrologic variables is discussed in Section 2.3.1.1.) Precipitation (RAING) is a scalar variable in EXAMS; a PCPLDG is therefore allowed only for compartments possessing an air-water interface. Non-zero PCPLDGs are automatically cancelled in the case of B (benthic) or H (hypolimnion) compartments. A PCPLDG is unconditionally permitted for compartment number 1, which will always have an air-water interface if the system definition rules discussed in Section 2.3.1.1 are followed. For all other water-column compartments, EXAMS simply looks back at the (J-1) compartment. If this (J-1) compartment is also part of the water column, it is assumed to be directly above the current (J) compartment and any non-zero PCPLDG is removed. Compartments with an air-water interface are always preceded by a benthic (B) compartment when EXAMS' system definition conventions (Section 2.3.1.1) are observed.

EXAMS' subroutine CKLOAD evaluates the propriety of the four kinds of loadings that enter via carrier flows. These loadings are evaluated against the volume of the carrier flows and the water quality characteristics of the target compartment. These evaluations were designed to prevent a user inadvertently specifying a loading outside EXAMS' operating range. In particular, EXAMS makes no provision for crystallization of the compound from solution, nor does the program allow for a gradual dissolution of chemical from a condensed (solid or liquid) phase. In addition, the non-linearities potentially present at high chemical concentrations (non-linear sorption isotherms, appreciable light absorption by the compound, zero-order biolysis, etc.) are not incorporated in the code. EXAMS' loading check computations are divided into two groups: checks based on carrier flows of water alone (PCPLDG and IFLLDG), and checks based on carrier flows of water plus an entrained sediment loading (STRLDG and NPSLDG).

Ground-water seep and rainfall loadings are simply constrained to the lesser of 50% of the aqueous solubility of the pollutant or 1.E-5 M in SH2. In these computations, the temperature (TCELG) and pH (PHG and POHG) of the target compartment receiving the load are used to compute (as appropriate) the solubilities of each ionic species of the compound, and the distribution of the pollutant among its ionic species (distribution coefficients ALPHA, computed as described in Section 2.2). EXAMS then computes the concentration of pollutant in the carrier flow. If the solubility criterion is exceeded, EXAMS reduces the load to the extent necessary to conform to one-half the upper limit of EXAMS' operating range, and notifies the user of the modification(s). The loadings are simply recomputed as the product of one-half the limiting concentration and the carrier flow rate, that is,

Eq. 2.151 LOAD(kg/hr) = 0.5 * LIMIT(kg/L) * INFLOW(L/hr) / BETA

where LIMIT is one-half the solubility of the least soluble chemical species or 1.E-5 M in SH2 (whichever is less), and BETA is the fraction of the total concentration present in the least soluble dissolved form.

Each streamflow (STFLDG) or non-point-source water flow (NPSFLG) entering a compartment may have an associated stream sediment (STSEDG) or non-point-source sediment (NPSEDG) loading (kg sediment/hr) to the compartment. STSEDG and NPSEDG are not used in transport computations (see Section 2.3.1.3). In the course of evaluating stream-borne and non-point-source pollutant loadings, EXAMS computes a sorption equilibrium for capture of the pollutant by entrained sediments in the stream or non-point-source flows entering each compartment. These computations use the temperature, pH, and sediment partitioning parameters (e.g., organic carbon content (FROCG) and ion exchange capacities (AECG and CECG)) of the target compartment. From the sediment/water ratio of the carrier flow, EXAMS computes the distribution coefficients (ALPHA) of the chemical in the carrier flow. If the residual aqueous concentration of any dissolved species exceeds its concentration limit, the offending loading is reduced via Eq. 2.151. Note that this reduced loading is less than the maximum permissible loading for the inlet stream.

After checking the loadings and making any necessary modifications, summing all external loads and units conversion from kg/hr to mg/hr yields term Le of Eq. 2.1.

"Drift" loadings (DRFLDG) are initially implemented without modification. If EXAMS' steady-state computations result in final chemical concentrations above EXAMS' operating range (i.e., residual aqueous dissolved concentrations greater than 50% of solubility or 1.E-5 M in SH2), any DRFLDGs are then sequentially reduced until the computationally invalid estimates are corrected. These computations are executed in subroutine STEADY. (If no drift loads were specified and the results are outside the operating range, EXAMS aborts the run and returns control to the user for corrective action.)

The DRFLDG vector can be used to specify miscellaneous loadings not encompassed in EXAMS' four other loading types. EXAMS, for example, does not allow for entry of pollutant across the air-water interface from a polluted atmosphere (Section 2.3.2). The impact of a polluted atmosphere can, however, be computed from the bulk atmospheric partial pressure of the contaminant, and entered into EXAMS via the DRFLDG vector. The net flux of pollutant across the air-water interface (F, moles/m2/hr) is given (Eq. 2.86) by:

$$F = Kl\ (Pg/H - Cl)$$

where Kl is the exchange constant (m/hr), and both (Pg/H) and Cl have units of (moles/m3). By assuming the bulk atmosphere to be uncontaminated (Pg = 0.0), the term (Pg/H) was discarded in the development of EXAMS' algorithm for computing volatilization losses of pollutants from aquatic systems. In much the same way, the gross pollutant loadings imposed by a contaminated atmosphere can be computed by taking Cl = 0.0. EXAMS computes and reports a contaminant-specific pseudo-first-order exchange constant (/hr) for each sector of the ecosystem. These values, representing (Kl * AREAG / VOLG) for each compartment, can be read off from EXAMS' output table "Kinetic Profile of Organic Toxicant" during a preliminary run of the program. The gross flux (F, moles/m2/hr) entering the system from a polluted atmosphere is

$$F = Kl\ (Pg/H)$$

Given the partial pressure of the compound in the bulk atmosphere, the loadings on the system (kg/hr) can thus be computed via:

$$DRFLDG = \frac{Kl * AREAG}{VOLG} * VOLG * MWTG * 0.001 * Pg * \frac{1}{HENRYG}$$

kg/hr   /hr   m3   g/mol   kg/g atm mol/(atm m3)

After computing DRFLDs for each sector of the system, EXAMS can be run again to evaluate the impact of the contaminated atmosphere. When interpreting EXAMS' outputs, however, it must be remembered that EXAMS' estimates of volatilization halflives and persistence assume that the atmosphere has been decontaminated.

Non-zero boundary conditions can also be loaded into EXAMS via the DRFLDG vector. EXAMS' environmental input data can include a characteristic length (CHARLG), cross-sectional area (XSTURG), and dispersion coefficient (DSPG) at any boundary of the system (by setting either JTURBG or ITURBG to zero, as described in Section 2.3.1.4). The exchange flow of water across the boundary is given by (Eq. 2.74):

$$FLOW\ (liters/hr) = \frac{(1000)(DSPG)(XSTURG)}{(CHARLG)}$$

If the inlet exchange flow is contaminated to a level of [C] mg/L, the loading (kg/hr) on the system of interest is simply:

$$LOAD = FLOW * [C] * 1.E{-}6\ (kg/mg)$$

This load can be imposed of the receptor compartment via the appropriate element of the DRFLDG vector. Remember, however, that the loading will be removed for EXAMS' persistence simulation.

The final term in Eq. 2.1 is "Li," the sum of the internal loadings on the system compartments. These loadings arise from flows of contaminated water, sediments, and plankton among the physical sectors (compartments) of the ecosystem. Their magnitudes can be computed from the magnitudes of the flows, the distribution of the compound among its dissolved and sorbed species, and the concentration of the pollutant in the source compartments (expressed as mass/unit aqueous volume). EXAMS uses the WATFL (L/hr) and SEDFL (kg/hr) flow matrices (see Section 2.3.1.5) to compute a matrix of internal loading factors (EXAMS' internal variable INTINL). Taking "S" as the compartment number (index) of the source compartment, and "T" as the index of the target comprtment, each element of INTINL is computed from:

Eq. 2.152
$$\mathrm{INTINL} = \mathrm{WATFL}(T,S)*\mathrm{ALPHA}(16,S) + \frac{\mathrm{SEDFL}(T,S)*\mathrm{ALPHA}(17,S)}{\mathrm{SEDCOL}(S)} + \mathrm{WATFL}(T,S)*\mathrm{ALPHA}(18,2)*\mathrm{PLRAG}(S)$$

where the total dissolved, sediment-sorbed, and biosorbed distribution coefficients of the source compartment are given by ALPHA(16,S), (17,S), and (18,S) respectively (Section 2.2.4). This computation results in terms which, when multiplied by the total concentration of pollutant in the source (S) compartments (mg/L), yield the mass loadings Li (mg/hr) on the target (T) compartments, the final term in Eq. 2.1.

2.5 Data Assembly and Solution of Equations

2.5.1 Exposure

After computing all terms in Eq. 2.1, the resulting system of mass-balance equations can be divided through by the volume of the compartments to give a set of equations describing the rate of change of chemical concentration over time:

Eq. 2.153
$$\frac{d[C]}{dt} = \frac{Le}{V} + \frac{Li}{V} - K\,[C]$$

As time passes, the system evolves toward an ultimate "steady-state" condition at which the concentrations achieve stable values. This endpoint is defined by the condition d[C]/dt = 0.0 for every compartment. At steady state, then, the concentration of pollutant in each sector of the ecosystem is given by

Eq. 2.154
$$[C] = (Le/V + Li/V)/K$$

EXAMS' subroutine STEADY was designed to solve the equations for these concentrations, which define the exposure levels of the pollutant.

The logic of the situation can be illustrated via an elementary example. For the example, consider the behavior of a non-sorbing chemical, subject to neutral hydrolysis as its sole transformation process, in a static one-hectare pond. The pond is 1 meter deep, with VOLG therefore 10000 m3. The benthic subsystem consists of a 5 cm active depth of material with a bulk density (SDCHRG) of 1.5 g/cc and a water content (PCTWAG) of 150%. The environmental volume of the benthic zone (VOLG) is 500 m3; its aqueous volume is 250000 liters of water (Eq. 2.12). Defining exchange between the benthic subsystem and the water column via XSTURG = 10000 m2, CHARLG = (1.05/2) = 0.525 m, and DSPG = 1.E-4 m2/hr, the rate of exchange of fluid volume between the water column and the interstitial pore water (Section 2.3.1.4) is

$$WATFL = \frac{250000}{500} * \frac{(1.E-4)(10000)}{0.525} = 952.4 \text{ liters/hr}$$

This exchange flow of water can be reduced to its pseudo-first-order effect on chemical concentrations (Kt) in the water column (w) and the benthic (b) subsystem via:

$$Kt(w) = 952.4/1.E7 = 9.524E-5 \text{ /hr}$$

and

$$Kt(b) = 952.4/250000 = 3.810E-3 \text{ /hr}$$

As the compound does not sorb, transport of sediment and plankton can in this instance be ignored.

The internal loadings on the system arise from pollutant contamination of the 952.4 L/hr exchange flow between the system compartments. All the compound is present in dissolved form, thus giving ALPHA(16) = 1.0 by definition. EXAMS computes its internal load factors Li/V by dividing the elements of INTINL (Eq. 2.152) by the volume of the target compartment. In this instance, the load factor on the benthic subsystem resulting from contamination of the water column is

INTINL(b,w) <--- (952.4 * 1.00)/250000 = 3.810E-3 /hr

and the load factor on the water column resulting from contamination of the benthic interstitial water is

INTINL(w,b) <--- (952.4 * 1.00)/1.E7 = 9.524E-5 /hr

(INTINL and Kt are equal in this much simplified example; this is not usually the case.)

Finally, given an external load on the water column (here a DRFLDG) of, say, 0.02 kg/hr, and a neutral hydrolysis rate constant of 0.01 /hr, the behavior of the chemical in the system is given by:

Eq. 2.155 d[Cw]/dt=(0.02E6/1.E7)+9.524E-5(Cb)-(0.01 + 9.524E-5)Cw

Eq. 2.156 d[Cb]/dt= 3.810E-3(Cw) - (0.01 + 3.810E-3)Cb

where Cw is the aqueous concentration in the water column and Cb is the aqueous concentration in the interstitial pore water (mg/L). At steady state, d[Cw]/dt = d[Cb]/dt = 0.0, resulting in 2 equations in 2 unknowns:

Eq. 2.157 - 0.01009524 Cw + 0.00009524 Cb = - 0.002

Eq. 2.158 0.00381 Cw - 0.01381 Cb = 0.0

This elementary example can be easily solved to give Cw = 0.1986 and Cb = 0.0548 mg/L. EXAMS' subroutine STEADY solves the simultaneous linear equations that describe steady-state concentrations by use of the Gaussian elimination algorithm discussed in Section 2.3.1.2. EXAMS' output for the example system described above is given in Table 2.26.

Table 2.26. EXAMS' output tabulation of steady-state concentrations.

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Unsorbed chemical subject to neutral hydrolysis
ECOSYSTEM: Static 1-hectare pond, 1 meter deep
-------------------------------------------------------------------------
TABLE 13. DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
-------------------------------------------------------------------------
COMP STEADY-STATE RESIDENT MASS    **** TOXICANT CONCENTRATIONS ****
       2                           TOTAL   DISSOLVED SEDIMENTS   BIOTA
     G/M        KILOS         %    MG/*       MG/L      MG/KG     UG/G
--- ------     ------    ------ --------- --------- --------- ---------
  1 0.199       1.986    100.00 0.199     0.199     0.000     0.000
 SUBTOTAL:      1.986     99.32
 AND IN THE BOTTOM SEDIMENTS:
  2 1.370E-03 1.3699E-02 100.00 2.740E-02 5.479E-02 0.000     0.000
 SUBTOTAL:    1.3699E-02   0.68
TOTAL MASS (KILOGRAMS) =     2.000
-------------------------------------------------------------------------
* TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.
```

As Gaussian elimination is not an infallible mechanism for executing these computations, EXAMS' subroutine STEADY includes a second technique for computing the solution to the system of equations (Eq. 2.154). This algorithm is an iterative method that applies Eq. 2.154 to each compartment in turn, and then repeats the entire process until such time as the successive estimates for each compartment change by less than 0.0001%. This alternative algorithm is invoked in those cases for which Gaussian elimination fails.

EXAMS allows for up to 100000 interations of the full "linear cascade" computation. If the linear cascade terminates without full convergence, EXAMS aborts the run; this event generally can be taken as an indication that steady-state concentrations are unbounded. For example, a non-transformable chemical in a static pond without any export pathways will accumulate indefinitely; in this situation no "steady-state" condition can be computed. The user can check on the degree of convergence achieved by EXAMS for the full ecosystem by examining the mass balance check printed as the final entry ("Residual Accumulation Rate") in EXAMS' output table entitled "Analysis of Steady-State Fate of Organic Toxicant."

In the elementary example given above, the linear cascade solution would proceed:

Iteration 1, step 1: solve for Cw (compartment number 1)

$$Cw = (Le/V + Li/V)/K = (0.002 + 9.524E{-}5(Cb)) / 0.01009524$$

giving, as Cb at the moment = 0.0,

$$Cw = 0.002/0.01009524 = 0.19811$$

Iteration 1, step 2: solve for Cb (compartment number 2)

$$Cb = (Le/V + Li/V)/K = 0.00381(Cw)/0.01381$$

$$= (0.00381*0.19811)/0.01381 = 0.05467$$

From the initial estimates, the second iteration proceeds to compute a refined estimate of Cw and Cb:

$$Cw = (0.002 + (9.524E{-}5*0.05467))/0.01009524 = 0.19863$$

$$Cb = (0.00381*0.19863)/0.01381 = 0.054799$$

The convergence test is computed for each compartment by calculating the relative change in the estimate. The change in Cw was

$$1 - 0.19811/0.19863 = 0.0026$$

and the change in Cb was

$$1 - 0.05467/0.054799 = 0.0026$$

As these test values are greater than EXAMS' convergence criterion (1.E-6), EXAMS continues with a third iteration of the linear cascade. EXAMS judges convergence to be complete only when the relative change in every compartment is less than 1.E-6.

2.5.2 Fate

After computing the ultimate exposure concentrations that will be produced in the system, EXAMS executes an evaluation of the impact of each transport and transportation process on the behavior of the compound. During the course of reducing its input data to pseudo-first- order form, EXAMS preserves the value of each process' contribution to the overall pseudo-first-order rate constant K (Eq. 2.1) for each compartment. The flux of chemical transformed or transported under steady-state conditions (mass/time) is then given by the product of the process rate constant, the steady-state concentrations, and the aqueous volume of each compartment. In the instance under review, the chemical fluxes attributable to neutral hydrolysis are

$$Fw = Khyd * Cw * WATVOL(w) * 1.E-6 \ (kg/mg)$$

$$= (0.01)(0.1986)(1.E7)(1.E-6) = 0.01986 \ kg/hr$$

in the water column, and

$$Fb = (0.01)(0.05479)(2.5E5)(1.E-6) = 0.000137 \ kg/hr$$

in the benthic subsystem.

EXAMS sums the fluxes (by process) over the entire system, and computes the significance of the process via division of the process flux by the sum of the external loadings on the system, followed by conversion of this result to a percentage basis. In the example, the total flux is (0.01986 + 0.000137) kg/hr, the total loading was 0.02 kg/hr, thus hydrolytic transformation accounts for 100(0.01986 + 0.000137)/0.02 = 100% of the input loadings, as of course it must in this elementary example.

EXAMS' output table containing the results of the flux analysis, entitled "Analysis of Steady-State Fate of Organic Toxicant," also includes estimated halflives for removal or dissipation of the chemical from the system. These halflives are computed under the assumption that internal transport delays are insignificant and, thus, are intended solely as a supplemental view of the general significance of each process. The halflife computations are executed via division of the total process fluxes by the total mass of pollutant resident in the system to give a system-wide pseudo-first-order rate constant Kpr. The halflife is then simply

$$Tp = - \ln(0.5)/Kpr$$

In the example case, the total resident mass (computed as the sum of volumes and concentrations) is 2.00 kg (Table 2.26), and the projected hydrolytic halflife is therefore

$$Tp = (0.69315 * 2.00)/(0.01986 + 0.000137) = 69.3 \text{ hours.}$$

EXAMS does not always and inevitably report fluxes and halflives in hours, for in many instances the hour is an inconveniently small reporting unit. Instead, the program makes a preliminary evaluation of the total transport and transformation flux through the ecosystem, and computes a first-order estimate of the total halflife of the compound. This preliminary estimate is then used to select the most appropriate (hours, days, months, or years) time scale for reporting the results of all succeeding time-dependent computations. This estimate of the "system-level" halflife is also used to set the time intervals for EXAMS' "persistence" computations, as described in Section 2.5.3.

EXAMS' flux computations, along with its table of compartment- specific pseudo-first-order rate constants (output table "Kinetic Profile of Organic Toxicant") were designed to serve as a "sensitivity analysis" of the behavior of the pollutant in the particular ecosystem involved. These tables indicate the relative strength of the transformation processes, and thereby indicate which processes are in need of the most scrupulous and exact experimental determinations of rate constants. In addition, EXAMS interactive capabilities allow a user to vary the input data over a reported error bound, and thus determine, for example, the degree of uncertainty implied for steady- state exposure concentrations.

2.5.3 Persistence

EXAMS' final round of computations deal directly with a third (after exposure and fate) aspect of pollutant evaluation in aquatic systems, that of the "persistence" of the compound. It should perhaps be emphasized that EXAMS computes local, rather than global, persistence, that is, EXAMS' computations address the persistence of compounds in the specific ecosystem under review, and do not address the global issue of the persistence of a compound after it leaves the local ecosystem. Thus, for example, a compound that is not subject to any transformation processes is (globally) totally persistent by definition. Within the more limited context of a particular ecosystem, however, export processes will ultimately result in a "cleanup" of the system, and the time required for this cleanup process can be computed. (As the ultimate exposure concentrations for a transformationally persistent chemical in a static (closed) system are unbounded, EXAMS never encounters the resulting infinite cleanup times.)

EXAMS begins its persistence computations by using the steady-state concentrations of pollutant in the system as a set of starting values or "initial conditions." These initial conditions are presented to a numerical integration package (subroutine DRIVER et seq.). The relevant set of differential equations, describing the behavior of the pollutant over time, is essentially Eq. 2.1 with the external loadings (Le) set to zero or struck from the equations:

Eq. 2.159 $$d[C]/dt = Li/V - K[C]$$

EXAMS computes the dissipation of the compound over time, taking the time required to encompass 2 (estimated) system-level halflives as the endpoint of the simulation. The results of this simulation are summarized in EXAMS' output table entitled "Simulation of System Response after Load Ceases."

EXAMS' subroutine DRIVER has two integration packages available to it; these routines have been described by Malanchuk, Otis, and Bouver (1980). DRIVER initially calls upon a 4th-5th order variable time-step Runge-Kutta integrator. In the event that the equations are mathematically "stiff," the partially complete integration is returned to DRIVER, which then invokes an alternate package that integrates stiff equations by Gear's method.

EXAMS limits the expense incurred in the integration via a limitation on the total number of steps which these routines are permitted to execute. EXAMS writes out the secular dissipation of the compound at 12 equally spaced times, up to the endpoint (TFINAL) defined by 2 estimated system-level halflives. If the integrators exceed their alloted expense allowance prior to integration to TFINAL, control is returned to DRIVER for evaluation fo the situation. If the integrators have failed to reach the first output point (TFINAL/12), EXAMS aborts all further peristence computations and so notifies the user. If at least one output point has been passed, EXAMS uses the latest point reached by the integrators in its persistence computations, and notifies the user that the dissipation simulation was abbreviated.

In the vast majority of cases, EXAMS' dissipation simulations conclude with a successful integration to TFINAL. EXAMS' output summary of the time course of dissipation via neutral hydrolysis in the static pond used as an example in Section 2.5.1 is given in Table 2.27.

Table 2.27. Sample EXAMS output for dissipation of chemical after removal of external loadings

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Unsorbed chemical subject to neutral hydrolysis
ECOSYSTEM: Static 1-hectare pond, 1 meter deep
------------------------------------------------------------------
TABLE 16.  SIMULATION OF SYSTEM RESPONSE AFTER LOAD CEASES.
------------------------------------------------------------------
TIME       AVERAGE POLLUTANT CONCENTRATIONS          MASS OF POLLUTANT
-----      --------------------------------          -----------------
HOURS    WATER COLUMN          BOTTOM SEDIMENTS     WATER COL   SEDIMENTS
     -------------------   -------------------   ---------   ---------
     FREE(MG/L) SED(MG/KG)  PORE(MG/L) SED(MG/KG)  TOTAL KG    TOTAL KG

  0.  0.199       0.000       5.479E-02  0.000      1.986      1.370E-02
 12.  0.176       0.000       5.430E-02  0.000      1.760      1.357E-02
 24.  0.156       0.000       5.298E-02  0.000      1.560      1.324E-02
 36.  0.138       0.000       5.107E-02  0.000      1.383      1.277E-02
 48.  0.123       0.000       4.875E-02  0.000      1.225      1.219E-02
 60.  0.109       0.000       4.616E-02  0.000      1.086      1.154E-02
 72.  9.627E-02   0.000       4.341E-02  0.000     0.9627      1.085E-02
 84.  8.533E-02   0.000       4.060E-02  0.000     0.8533      1.015E-02
 96.  7.563E-02   0.000       3.778E-02  0.000     0.7563      9.444E-03
108.  6.704E-02   0.000       3.500E-02  0.000     0.6704      8.751E-03
120.  5.943E-02   0.000       3.232E-02  0.000     0.5943      8.079E-03
132.  5.268E-02   0.000       2.974E-02  0.000     0.5268      7.434E-03
144.  4.670E-02   0.000       2.728E-02  0.000     0.4670      6.820E-03
```

EXAMS' subroutine SUMUP prints a summary of the exposure and fate information generated by the program and also estimates and reports the length of time required for cleanup of the ecosystem. EXAMS reports, in the first instance, the percentage of the initial chemical masses in the entire water column and benthic subsystem that had been dissipated by time TFINAL. EXAMS then weights these dissipations according to the initial distribution of the chemical in the system, and reports a first-order estimate of the time required for the system to cleanse itself of the chemical mass accumulated at steady state. This estimate is computed as 5 (pseudo-first-order, weighted) halflives; in a true first-order system this would correspond to dissipation of 97% of the mass of chemical initially present in the system. (The actual (mathematical) "order" of the system is defined by the number of compartments used to describe the ecosystem. For example, when a water-body is described to EXAMS via 20 segments, EXAMS compiles 20 linked first-order differential equations, and solves this system of equations to generate its outputs. The data used in EXAMS' persistence time computations is generated by summing the residual chemical masses over compartments, thereby following the dissipation of the chemical in the entire system. The computations are in this sense reduced order approximations; thus EXAMS reports are given as "rough" estimates (e.g., Table 2.28).)

This computation can be illustrated via the results of the sample simulation given in Table 2.27. At the expiration of 144 hours, the resident pollutant mass had fallen from 1.986 to 0.467 kg in the water column. This dissipation of the pollutant represents a loss of

$$100\ (1 - (0.467/1.986)$$

or 76.5% of the original material. Similarly, the benthic subsystem has lost (1.37E-2 - 6.82E-3) = 6.88E-3 kg or 50.2% of its original mass of chemical. (The benthic sediment exhibits a slower loss of chemical as a result of continuing recontamination (Li, Eq. 2.159) of this subsystem from the water column.)

In a first-order system, the decrease of an initial mass of material Qo over time is given by

$$Q(t) = Qo \exp(-k * t)$$

or

$$\ln(Q(t)/Qo) = -kt$$

where k is the first-order rate constant and t is time. The halflife is defined as the time required for Q(t) to reach Qo/2 or for Q(t)/Qo = 0.5, that is,

$$H = -\ln(0.5)/k$$

The first-order halflives (H) for these water-column (Hw) and benthic (Hb) subsystems are, therefore:

$$Hw = (0.69315)(144) / \ln(.467/1.986) = 69.0 \text{ hrs}$$

and

$$Hb = (0.69315)(144) / \ln(6.82E-3/1.37E-2) = 143.4 \text{ hrs}$$

At steady state, 99.32% of the compound was present in the water column, and only 0.68% was in the benthic subsystem (Table 2.26). EXAMS thus estimates the time required for dissipation of the chemical as:

$$Td = 5\ (0.9932\ (Hw) + 0.0068\ (Hb))$$

$$= 5\ (0.9932\ (69.0) + 0.0068\ (143.4)) = 347.5 \text{ hrs}$$

or 14.5 days. EXAMS output summary for this example is given in Table 2.28.

Table 2.28. Sample EXAMS summary output table, analysis of unsorbed compound subject to neutral hydrolysis, in static 1 hectare pond

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Unsorbed chemical subject to neutral hydrolysis
ECOSYSTEM: Static 1-hectare pond, 1 meter deep
-------------------------------------------------------------------------
TABLE 17.  EXPOSURE ANALYSIS SUMMARY.
-------------------------------------------------------------------------
EXPOSURE:
 A. MAXIMUM CONC. IN WATER COLUMN: 0.20     MG/L DISSOLVED, 0.20     TOT
    MAX. CONC. IN BOTTOM SEDIMENT: 5.48E-02 MG/L DISSOLVED IN PORE WATER
 B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON: 0.00     UG/G
                                       BENTHOS:  0.00     UG/G
 C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS: 2.74E-02 MG/KG (DRY WEIGHT)
FATE:
 A. TOTAL STEADY-STATE ACCUMULATION:  2.0     KG; 99.32% IN WATER COL.,
       0.68% IN BOTTOM SEDIMENTS.
 B. TOTAL LOAD: 2.00E-02 KG/HOUR - DISPOSITION: 100.00% VIA CHEMICAL
      TRANSFORMATIONS,   0.00% BIOTRANSFORMED,   0.00% VOLATILIZED,
       0.00% EXPORTED VIA OTHER PATHWAYS.
PERSISTENCE:
 A. AT THE END OF A  144.     HOUR RECOVERY PERIOD, THE WATER COLUMN HAD
      LOST  76.49% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD
      LOST  50.21% OF THEIR INITIAL BURDEN (  76.31% REMOVAL OVERALL).
 B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY 14. DAYS.
```

If the majority of the chemical had been present in the benthic zone, EXAMS would of course have given computational precedence to dissipation in the sediment subsystem for its estimate of decontamination time.

A more detailed evaluation of the persistence of the chemical can be executed via a graphical analysis of the time course of pollutant dissipation, plotted from the results of EXAMS' numerical simulation of this phenomenon (Table 2.27). In interpreting EXAMS' estimate of the time required to dissipate the chemical, it should be remembered that EXAMS' estimate represents five halflives, or about 97% removal of the initial mass. If this removal suggests that the chemical would still occur at unacceptable concentrations, a first-order evaluation of the time required to achieve a specified reduction can be computed from EXAMS' outputs. Suppose, for example, that the time to reduce the chemical to 0.01% of its initial value were the time of interest. This time is given by the expression

(-ln(Q/Qo)/K), where Q/Qo is in this case 0.0001. EXAMS' estimate of decontamination time is computed as (5)(0.69315)/K, where K can be regarded as a weighted whole-system first-order decay constant. EXAMS' estimate of dissipation time Td can thus be expanded via the approximation:

Eq. 2.160
$$T = \frac{-\ln(Q/Qo)\ Td}{(5)(0.69315)}$$

In this instance, Q/Qo = 0.0001, -ln(Q/Qo) = 9.21, and the time to reduce the chemical to 0.01% of its steady-state value is approximately

$$T = \frac{(9.21)(14)}{(5)(0.69315)} = 37 \text{ days}$$

Note, however, that a continued first-order decay of chemical in the benthic subsystem would, at 37 days (888 hours), result in a residual of

$$100 \exp(888\ (\ \ln 0.5\ /\ Hb)\ )$$

or 1.4% of the original benthic pollutant mass. The system-wide dissipation of the chemical may leave pockets of higher concentration in zones of restricted physical transport.

Extrapolations of EXAMS' results beyond the designed operating range of the program are probably ill-advised. If necessary, however, a plot of the results of EXAMS' dissipation simulation should be used to evaluate the propriety of a first-order extrapolation of system self-purification times.

SECTION 3

USER'S GUIDE

3.1 Introduction and Sample Run

This Section is an introduction to the use of the EXAMS interactive language and system. It is designed to familiarize users with the structure of the command language that gives access to the computer system, to describe the kinds of input and output used by the system, and to provide some sample sessions that serve as tutorials and as examples of EXAMS applications. Sample data input forms for organizing and preparing chemical and environmental data for entry into the program can be found at the end of Section 3.1.

3.1.1 Introduction

This version of EXAMS was designed to evaluate the ultimate or "steady-state" behavior of organic chemicals in aquatic ecosystems. EXAMS is not a "model" of aquatic ecosystems, for it contains but a single state variable -- a vector of concentrations of chemical pollutants. The properties of aquatic ecosystems that govern the behavior of synthetic organic chemicals are presented to EXAMS via an n-compartment set of input data. EXAMS uses these data to compute the behavior of chemical pollutants in the ecosystem. The environmental descriptors encompass only those variables having a direct bearing on pollutant behavior; they can thus be termed a "canonical" description of the environment. Each environmental variable is constrained to a single value within a given area (compartment) of the ecosystem, and thus must be regarded as an average or "typical" value over some relevant period.

EXAMS couples the canonical characteristics of the environment to the properties of a given organic chemical, using process models (mathematical relationships) appropriate to each aspect of chemical behavior considered (Section 2). EXAMS' process models include the kinetics of volatilization, transport, direct photolysis, hydrolysis (specific-acid/base and neutral), oxidation, and bacterial transformations in the water column and bottom sediments of the ecosystem, as well as equilibrium partitioning of the chemical into (as many as five) ionic species, each of which may occur as a dissolved, sediment-sorbed, or biosorbed molecule.

The process models are assembled into a set of ordinary, first-order differential equations that describe the kinetics of the chemical in the n-compartment system under investigation. EXAMS then analyzes this set of differential equations in several ways. EXAMS produces a series of output tables that provide information on the fate, exposure, and persistence of the chemical, and provide some guidance for exploring the degree to which conclusions drawn from the data are affected by error or uncertainty in the input data (sensitivity).

A number of operational definitions can be attached to the notions of "fate," "exposure," etc. For EXAMS' purposes, the "fate" of a pollutant means its ultimate (steady-state) relative distribution within the ecosystem (percent captured by bottom sediments, etc.), and the percentage of the total system loading that is consumed by each kinetic process (photolysis, export, etc.) at steady state. "Exposure" is taken to mean the final residual concentration of chemical present in each compartment at steady state. Exposure concentrations are presented in four forms: the total concentrations (mg/L in the water column, mg/kg in bottom sediments), concentrations of dissolved species (mg/L), sediment-sorbed concentrations (mg/kg), and biosorbed concentrations (ug/g) associated primarily with planktonic or sessile organisms that form the base of the food chain.

The "persistence" of the chemical is evaluated via an additional set of operations. The input loadings are set to zero (removed) and the system of equations is passed to a numerical integration subroutine with the steady-state concentrations as initial values. The integrator then computes the disappearance of the chemical from the ecosystem over a period corresponding to about 2 system half-lives, i.e., the time needed to remove about 75% of the chemical accumulated in the ecosystem. The outcome of this integration is reported to the user, and a "system self-purification time" is estimated from the results.

EXAMS does not undertake any formal sensitivity analyses of the system. Sufficient information is provided, however, to allow a user to derive the probable magnitude of uncertainties in conclusions that are implied by a given range or error bound for any of the input data. The computer outputs include a "Kinetic Profile" (or frequency scaling) of the chemical, with all processes reduced to equivalent (/hr) units, and a tabular presentation of the steady-state fate of the chemical (i.e., the percentage of the load consumed in each process). These tables indicate the relative importance of each transformation process within the ecosystem of concern. EXAMS' interactive capabilities allow the user to select the dominant process(es) and vary the relevant input data over a reported error range. In this way the effect, for example, of error in chemical rate constants on exposures and persistence can be readily evaluated.

3.1.2 Sample Run

A simple example EXAMS session is given below, including the initial LOGIN and LOGOUT sequences on the Athens Environmental Research Laboratory's DEC PDP 11/70 computer. The example shows the selection of benzo[f]quinoline and a eutrophic lake as the compound and ecosystem of concern, specification of chemical loadings, retrieval of a hard-copy of the results, and the computer output from the run. (The input data used for this example is also supplied with the batch version of the program.)

A series of sample data entry forms follow the output tables from the sample run. These forms (pp. 162-172) can be removed from the manual and duplicated; they provide a means of organizing and assembling input data for the EXAMS program.

```
PDS> @TSO
User TSO  UIC[250,203] TT13: 14:50:50 11-JAN-81

PDS> RUN EXAMS
14:51:34
          Welcome to EXAMS
   EXposure Analysis Modeling System
Athens Environmental Research Laboratory
    Released for field trials Jan-81


The ATHENS collection of compounds is available for your use.


EXAMS > COMPOUND IS BFQ

Compound selected > BENZO[f]QUINOLINE

EXAMS > ENVIRONMENT IS EUTROPHIC LAKE

Selected environment is: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE
                         TEST DEFINITION

EXAMS > CHANGE STRLD(1) TO 0.5

EXAMS > CHAN PCPLDG(1) TO 6.4E-03

EXAMS > CH PCPL(3) TO .032
EXAMS > CH PCP(6) TO 0.0064

EXAMS > CH IFLL(2) TO .02

EXAMS > CH IFLLDG(7) TO .02

EXAMS > CH NPSL(1) TO .16

EXAMS > CHANGE NPSLDG(6) TO 0.16

EXAMS > RUN

Simulation beginning for:
Compound: BENZO[f]QUINOLINE
Environment: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST
 DEFINITION
with a load of (kg/hr) >   0.904800

Run complete.

EXAMS > PRINT ALL

Requested report has been spooled to printer.

EXAMS > STOP
        Job433 -- STOP
14:57:19  Size: 32K   CPU: 22.35  Status: SUCCESS

PDS> LOGOUT
        User TSO  UIC [250,203] TT13: 14:48:00 11-JAN-81
CONNECT TIME 07 M  SYSTEM UTILIZATION 43 MCTS
```

The seventeen output tables generated by this sample session are given on the following nine pages.

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
-----------------------------------------------------------------------------
TABLE 1.1.  SH2 (NEUTRAL MOLECULE, SPECIES  1) INPUT DATA.
MWT=  179.2      SOL =  76.10       VAPR= 2.8000E-05 HENRY= 0.0000
KVO= 2.2000E-04 ESOL= 0.0000        EVPR= 0.0000     EHEN  = 0.0000
KPS=  1300.      KPB  =  500.0      KOC  = 0.0000     KOW   = 0.0000
KAH1= 0.0000      EAH1= 0.0000        KNH1= 0.0000      ENH1= 0.0000
KAH2= 0.0000      EAH2= 0.0000        KNH2= 0.0000      ENH2= 0.0000
KAH3= 0.0000      EAH3= 0.0000        KNH3= 0.0000      ENH3= 0.0000
KBH1= 0.0000      EBH1= 0.0000        KOX1= 0.0000      EOX1= 0.0000
KBH2= 0.0000      EBH2= 0.0000        KOX2= 0.0000      EOX2= 0.0000
KBH3= 0.0000      EBH3= 0.0000        KOX3= 0.0000      EOX3= 0.0000
KBACW1= 3.6000E-08 QTW1=  2.000       KBACS1= 3.6000E-08 QTS1=  2.000
KBACW2= 0.0000      QTW2= 0.0000       KBACS2= 0.0000      QTS2= 0.0000
KBACW3= 0.0000      QTW3= 0.0000       KBACS3= 0.0000      QTS3= 0.0000
KDP= 0.0000      RFLAT=  40.00      LAMAX=   298.00
QUANT1= 1.4000E-02 QUANT2= 0.0000      QUANT3= 0.0000
ABSORPTION SPECTRUM (ABS):      3984.        3910.        2056.
  1380.        1120.        1048.        1310.        1586.        1396.
  1332.        1454.        3008.        1584.        1350.        57.00
  15.60        16.70       0.0000       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
```

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
-----------------------------------------------------------------------------
TABLE 1.2.  SH3+ (SINGLY CHARGED CATION, SPECIES  2) INPUT DATA.
PKB1=  8.850      EPKB1= 0.0000       SOL=  761.0       ESOL= 0.0000
MWT =  179.2      KPS  =  130.0       KPB=  50.00       KCEC= 0.0000
KAH1= 0.0000      EAH1= 0.0000        KNH1= 0.0000      ENH1= 0.0000
KAH2= 0.0000      EAH2= 0.0000        KNH2= 0.0000      ENH2= 0.0000
KAH3= 0.0000      EAH3= 0.0000        KNH3= 0.0000      ENH3= 0.0000
KBH1= 0.0000      EBH1= 0.0000        KOX1= 0.0000      EOX1= 0.0000
KBH2= 0.0000      EBH2= 0.0000        KOX2= 0.0000      EOX2= 0.0000
KBH3= 0.0000      EBH3= 0.0000        KOX3= 0.0000      EOX3= 0.0000
KBACW1= 3.6000E-08 QTW1=  2.000       KBACS1= 3.6000E-08 QTS1=  2.000
KBACW2= 0.0000      QTW2= 0.0000       KBACS2= 0.0000      QTS2= 0.0000
KBACW3= 0.0000      QTW3= 0.0000       KBACS3= 0.0000      QTS3= 0.0000
KDP= 0.0000      RFLAT=  40.00
QUANT1= 1.4000E-02 QUANT2= 0.0000      QUANT3= 0.0000
ABSORPTION SPECTRUM (ABS):      3621.        3910.        3328.
  3197.        2937.        3047.        3127.        2858.        2668.
  2059.        1999.        3190.        3038.        4076.        2983.
  2578.        1216.        665.0       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
```

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
---------------------------------------------------------------------
TABLE 2.  INPUT DATA DESCRIBING ENVIRONMENT: GLOBAL PARAMETERS.
---------------------------------------------------------------------
KOUNT=  7     RAIN(MM/MO)=  105.0     CLOUD(10THS)=  5.0      LAT= 40.00
IRRADIANCE (WLAM,P/SQ CM/SEC/N NM):  8.9100E+10  3.3800E+11  1.1100E+12
 2.9900E+12  5.4000E+12  8.8400E+12  1.3800E+13  1.8500E+13  2.3300E+13
 2.8100E+13  5.2100E+13  1.8100E+14  2.1100E+14  2.2600E+14  2.4100E+14
 2.6800E+14  2.9400E+14  3.6600E+14  5.2600E+14  6.9200E+14  7.1200E+14
 6.8800E+14  8.1400E+14  9.1700E+14  9.2700E+14  9.5900E+14  9.8300E+14
 9.3000E+14  9.4900E+14  1.0000E+15  1.0500E+15  1.0600E+15  1.0700E+15
 1.0800E+15  1.0800E+15  1.0800E+15  1.0700E+15  1.0300E+15  9.8800E+14
---------------------------------------------------------------------
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  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
---------------------------------------------------------------------
TABLE 3.  INPUT DATA DESCRIBING ENVIRONMENT: BIOLOGICAL PARAMETERS.
---------------------------------------------------------------------
   TY   BIOMS        PLRA       BIOTM        BACTO      ACBAC       CHL
         (1)         (2)        DEG C.        (3)        (2)        MG/L
---------------------------------------------------------------------
   1L   51.00     2.0000E-02   20.00      1.0000E+05   1.000   4.0000E-03
   2B   250.0     0.0000       20.00      2.0000E+07   1.000
   3E   2.200      1.000       20.00      1.0000E+04   1.000   4.0000E-03
   4H  0.7500      1.000       5.000       1000.       1.000   5.0000E-04
   5B   10.00     0.0000       5.000      2.0000E+06   1.000
   6L   51.00     2.0000E-02   20.00      1.0000E+05   1.000   4.0000E-03
   7B   250.0     0.0000       20.00      2.0000E+07   1.000
---------------------------------------------------------------------
 (1) UNITS: MG/L IN WATER COLUMN (L,H,B); G (D.W.)/SQUARE METER IN (B).
 (2) DIMENSIONLESS NUMBERS.
 (3) UNITS: CELLS/ML IN L, E, H; CELLS/100 G D.W. IN B.
```

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  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
------------------------------------------------------------------------
TABLE 4.  INPUT DATA DESCRIBING ENVIRONMENT: DEPTHS AND INFLOWS.
------------------------------------------------------------------------
   TY    DEPTH        STFLO       STSED       NPSFL       NPSED      INTFL
           M        CU M/HR       KG/HR      CU M/HR      KG/HR     CU M/HR
------------------------------------------------------------------------
   1L    5.000        485.0       40.00       48.50       97.00
   2B   5.0000E-02                                                  130.0
   3E    10.00
   4H    10.00
   5B   5.0000E-02                                                  130.0
   6L    5.000                                48.50       97.00
   7B   5.0000E-02                                                  130.0
------------------------------------------------------------------------
```

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  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
------------------------------------------------------------------------
TABLE 5.  INPUT DATA DESCRIBING ENVIRONMENT: SEDIMENT CHARACTERISTICS.
------------------------------------------------------------------------
   TY    SDCHR       PCTWA       FROC          CEC        AEC         DOC
          (1)         (2)         (3)          (4)        (4)         MG/L
------------------------------------------------------------------------
   1L   0.5000                3.8000E-02    25.00      25.00       2.500
   2B    1.850       137.0    3.8000E-02    25.00      25.00
   3E   0.5000                3.8000E-02    25.00      25.00       2.500
   4H   0.5000                3.8000E-02    25.00      25.00      0.5000
   5B    1.850       137.0    3.8000E-02    25.00      25.00
   6L   0.5000                3.8000E-02    25.00      25.00       2.500
   7B    1.850       137.0    3.8000E-02    25.00      25.00
------------------------------------------------------------------------
 (1) UNITS: MG/L SUSPENDED SEDIMENT IN L, E, H; BULK DENSITY (G/CC) IN B
 (2) 100 * F.W./D.W. IN B.
 (3) DIMENSIONLESS.
 (4) MEQ/100 GRAMS DRY WEIGHT.
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  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
----------------------------------------------------------------------
TABLE 6.  INPUT DATA DESCRIBING ENVIRONMENT: AERATION, LIGHT, MISC.
----------------------------------------------------------------------
   TY     KO2         WIND       CMPET       DFAC       EVAP        AREA
      CM/HR @20  M/S @10 CM     /M         M/M       MM/MON       SQ M
----------------------------------------------------------------------
  1L    5.000       1.500      2.000      1.190      90.00     5.0000E+04
  2B                                                           5.0000E+04
  3E   10.00        2.000      2.000      1.190      85.00     2.5000E+05
  4H   0.0000      0.0000      1.000      1.190     0.0000     2.5000E+05
  5B                                                           2.5000E+05
  6L    5.000       1.500      2.000      1.190      90.00     5.0000E+04
  7B                                                           5.0000E+04
----------------------------------------------------------------------
```

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  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
----------------------------------------------------------------------
TABLE 7.  INPUT DATA DESCRIBING ENVIRONMENT: ADVECTIVE INTERCONNECTIONS.
----------------------------------------------------------------------
COMP. NO. (JFRAD)      1         3         6         2         5
CONNECTED (ITOAD)      3         6         0         1         4
ADVECTION (ADVPR)  1.00      1.00      1.00      1.00      1.00
COMP. NO. (JFRAD)      7         4
CONNECTED (ITOAD)      6         3
ADVECTION (ADVPR)  1.00      1.00
```

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
----------------------------------------------------------------------
TABLE 8.  INPUT DATA DESCRIBING ENVIRONMENT: TURBULENT INTERCONNECTIONS.

COMP. NO. (JTURB)       1          3          4          6          1
CONNECTED (ITURB)       2          4          5          7          3
X-SECTION (XSTUR)  5.000E+04  2.500E+05  2.500E+05  5.000E+04  2.500E+03
CHAR. LN. (CHARL)   2.53       10.0       5.03       2.53       300.
EDDY DISP. (DSP)   4.676E-05  0.398      9.306E-05  4.676E-05  1.196E+03

COMP. NO. (JTURB)       3
CONNECTED (ITURB)       6
X-SECTION (XSTUR)  2.500E+03
CHAR. LN. (CHARL)   300.
EDDY DISP. (DSP)   1.196E+03
```

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  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
-----------------------------------------------------------------------------
TABLE 9.  TRANSPORT PROFILE OF ECOSYSTEM.
-----------------------------------------------------------------------------
CP T*   VOLUME    SEDIMENT   WATER FLOW  SED. FLOW  RESIDENCE TIME (DAYS)
   Y  (CUBIC M)  MASS (KG) (CU. M/DAY) (KG/DAY)     WATER    SEDIMENTS
-----------------------------------------------------------------------------
  1L  2.500E+05   125.      2.552E+05  2.902E+04  0.980     4.308E-03
  2B  2.500E+03  3.376E+06  3.131E+03  3.001E+04  0.399      112.
  3E  2.500E+06  1.250E+03  7.367E+05   368.       3.39      3.39
  4H  2.500E+06  1.250E+03  2.423E+05  1.451E+05   10.3     8.613E-03
  5B  1.250E+04  1.688E+07  3.176E+03  1.500E+05   1.97      112.
  6L  2.500E+05   125.      2.628E+05  2.902E+04  0.951     4.307E-03
  7B  2.500E+03  3.376E+06  3.131E+03  3.001E+04  0.399      112.
-----------------------------------------------------------------------------
* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC
```

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  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
-----------------------------------------------------------------------------
TABLE 10.  KINETIC PROFILE OF ORGANIC TOXICANT.  RATE CONSTANTS DERIVED
FROM COUPLING OF TOXICANT CHARACTERISTICS TO ECOSYSTEM PROPERTIES.
-----------------------------------------------------------------------------
CP T*  ----------- PSEUDO-FIRST-ORDER RATE CONSTANTS (/HR) -----------
   Y  HYDROLYSIS PHOTOLYSIS OXIDATION  BIOLYSIS   VOLATILITY TRANSPORT
-----------------------------------------------------------------------------
  1L  0.000      3.925E-03  0.000      3.508E-03  1.374E-06  4.758E-02
  2B  0.000      0.000      0.000      5.750E-06  0.000      4.006E-04
  3E  0.000      2.010E-03  0.000      3.594E-04  1.192E-06  1.228E-02
  4H  0.000      1.690E-28  0.000      1.271E-05  0.000      7.161E-03
  5B  0.000      0.000      0.000      2.036E-07  0.000      3.765E-04
  6L  0.000      3.925E-03  0.000      3.508E-03  1.374E-06  4.882E-02
  7B  0.000      0.000      0.000      5.750E-06  0.000      4.006E-04
-----------------------------------------------------------------------------
* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC
```

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  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
----------------------------------------------------------------------------
TABLE 11.  CANONICAL PROFILE OF ECOSYSTEM.
----------------------------------------------------------------------------
CP T*  PH    POH  TEMP REAERATION COMPOSITE BACTERIAL  OXIDANT  DISSOLVED
   Y              DEG.   COEFF.   LIGHT AVE POP. SIZE  CONC.     PERCENT
   P               C.    M/HR         %     CELLS/**   (MOLAR)      %
----------------------------------------------------------------------------
  1L  8.00   6.00 20.0  5.000E-02  2.24     1.000E+05 1.000E-09  97.5
  2B  6.50   7.50 20.0  0.000     0.000     2.000E+07 0.000     2.955E-02
  3E  8.00   6.00 20.0  0.100      1.12     1.000E+04 1.000E-09  99.8
  4H  7.40   6.60  5.0  0.000     2.124E-28 1.000E+03 5.000E-10  99.9
  5B  6.50   7.50  5.0  0.000     0.000     2.000E+06 0.000     2.959E-02
  6L  8.00   6.00 20.0  5.000E-02  2.24     1.000E+05 1.000E-09  97.5
  7B  6.50   7.50 20.0  0.000     0.000     2.000E+07 0.000     2.955E-02
----------------------------------------------------------------------------
* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC
** ACTIVE BACTERIAL  POPULATIONS AS CELLS/ML IN WATER COLUMN,
   CELLS/100 G (DRY WEIGHT) OF SEDIMENTS IN BOTTOM SEDIMENTS.
```

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  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
----------------------------------------------------------------------------
TABLE 12.  TOXICANT LOADINGS (KG/HR) BY SYSTEM ELEMENT.
----------------------------------------------------------------------------
ELEMENT  STREAM FLOW    RAINFALL     INTERFLOW      NPS LOAD    DRIFT LOAD
-------  -----------   ----------   ----------    ----------    ----------
   1       0.5000      6.4000E-03                   0.1600
   2                                2.0000E-02
   3                   3.2000E-02
   4
   5
   6                   6.4000E-03                   0.1600
   7                                2.0000E-02
----------------------------------------------------------------------------
```

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  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
---------------------------------------------------------------------
TABLE 13. DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
---------------------------------------------------------------------
COMP STEADY-STATE RESIDENT MASS      **** TOXICANT CONCENTRATIONS ****
        2                             TOTAL   DISSOLVED SEDIMENTS   BIOTA
     G/M         KILOS          %     MG/*      MG/L      MG/KG      UG/G
--- ------      ------     ------ --------- --------- --------- ---------
  1 0.590        29.51       6.90 0.118     0.115      149.       57.4
  3 0.763        190.7      44.57 7.626E-02 7.613E-02  98.8       38.0
  4 0.750        187.5      43.84 7.501E-02 7.494E-02  96.9       37.3
  6 0.401        20.05       4.69 8.019E-02 7.815E-02  101.       39.0
 SUBTOTAL:       427.8      15.15
 AND IN THE BOTTOM SEDIMENTS:
  2  9.84        491.8      20.52  146.     0.116      145.       55.9
  5  6.22        1555.      64.88  92.1     7.367E-02  92.1       35.4
  7  7.00        349.9      14.60  104.     8.277E-02  103.       39.8
 SUBTOTAL:       2397.      84.85
TOTAL MASS (KILOGRAMS) =       2824.
---------------------------------------------------------------------
* TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.
```

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  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
---------------------------------------------------------------------
TABLE 14.  AVERAGE, MAXIMUM, AND MINIMUM CONCENTRATIONS AT STEADY STATE.
---------------------------------------------------------------------
  1
    CP)TOTAL       CP)DISSOLVED  CP)SEDIMENTS  CP)BIOTA       CP)MASS
                                                                    2
         MG/*           MG/L          MG/KG         UG/G          G/M
   ----------   ----------   ----------   ----------   ----------

WATER COLUMN:
AV       8.738E-02      8.606E-02        112.          42.9         0.63
MA   1) 0.118       1) 0.115      1)  149.      1)  57.4      3) 0.76
MI   4) 7.501E-02   4) 7.494E-02  4)  96.9      4)  37.3      6) 0.40

BOTTOM SEDIMENTS:
AV       114.           9.093E-02        114.          43.7          7.7
MA   2)  146.       2) 0.116      2)  145.      2)  55.9      2)  9.8
MI   5)  92.1       5) 7.367E-02  5)  92.1      5)  35.4      5)  6.2
---------------------------------------------------------------------
1 NUMBER IN HALF-PARENS CP) INDICATES COMPARTMENT WHERE VALUE WAS FOUND.
* TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.
```

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  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
-----------------------------------------------------------------------
TABLE 15.  ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.
-----------------------------------------------------------------------
               PROCESS                  MASS FLUX   % OF LOAD    HALF-LIFE*
                                         KG/DAY                    DAYS
          ------------------------      ---------   ---------    ---------
          HYDROLYSIS                    0.0000         0.00         ---
          OXIDATION                     0.0000         0.00         ---
          PHOTOLYSIS                     13.87        63.86       141.2
      ALL CHEMICAL PROCESSES             13.87        63.86       141.2
-----------------------------------------------------------------------
          WATER COLUMN (BACTERIA)        5.874        27.05        50.47
          BOTTOM SEDIMENTS (BACTERIA)   0.1237         0.57      1.3424E+04
      TOTAL BIOLYSIS                     5.998        27.62       326.4
-----------------------------------------------------------------------
          VOLATILIZATION                7.0866E-03     0.03      2.7625E+05
          WATER-BORNE EXPORT             1.842         8.48       1063.
-----------------------------------------------------------------------
TRANSFORMATION AND TRANSPORT             21.72       100.00
TOTAL SYSTEM LOAD                        21.72
RESIDUAL ACCUMULATION RATE:             5.7220E-06     0.00
-----------------------------------------------------------------------
* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.
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  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
---------------------------------------------------------------------------
TABLE 16.  SIMULATION OF SYSTEM RESPONSE AFTER LOAD CEASES.
---------------------------------------------------------------------------
TIME       AVERAGE POLLUTANT CONCENTRATIONS             MASS OF POLLUTANT
-----      --------------------------------             -----------------
DAYS     WATER COLUMN          BOTTOM SEDIMENTS      WATER COL    SEDIMENTS
      --------------------  --------------------  ---------    ---------
      FREE(MG/L) SED(MG/KG)  PORE(MG/L) SED(MG/KG)  TOTAL KG     TOTAL KG

  0.  8.606E-02   112.       9.093E-02   114.        427.8       2.397E+03
 15.  4.802E-02   62.3       8.613E-02   108.        285.6       2.323E+03
 30.  4.068E-02   52.8       8.024E-02   100.        242.8       2.211E+03
 45.  3.723E-02   48.3       7.454E-02   93.2        223.3       2.095E+03
 60.  3.483E-02   45.2       6.925E-02   86.6        210.1       1.984E+03
 75.  3.280E-02   42.5       6.439E-02   80.5        198.9       1.878E+03
 90.  3.095E-02   40.1       5.994E-02   74.9        188.7       1.779E+03
105.  2.923E-02   37.9       5.585E-02   69.8        179.1       1.686E+03
120.  2.762E-02   35.8       5.210E-02   65.1        170.0       1.598E+03
135.  2.612E-02   33.9       4.865E-02   60.8        161.5       1.515E+03
150.  2.471E-02   32.0       4.548E-02   56.8        153.4       1.437E+03
165.  2.339E-02   30.3       4.255E-02   53.2        145.7       1.363E+03
180.  2.214E-02   28.7       3.985E-02   49.8        138.5       1.293E+03
```

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  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: BENZO[f]QUINOLINE
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
---------------------------------------------------------------------------
TABLE 17.  EXPOSURE ANALYSIS SUMMARY.
---------------------------------------------------------------------------
EXPOSURE:
 A. MAXIMUM CONC. IN WATER COLUMN: 0.12     MG/L DISSOLVED, 0.12     TOT
    MAX. CONC. IN BOTTOM SEDIMENT: 0.12     MG/L DISSOLVED IN PORE WATER
 B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON:  57.      UG/G
                                       BENTHOS:   56.      UG/G
 C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS: 1.46E+02 MG/KG (DRY WEIGHT)
FATE:
 A. TOTAL STEADY-STATE ACCUMULATION: 2.82E+03 KG; 15.15% IN WATER COL.,
       84.85% IN BOTTOM SEDIMENTS.
 B. TOTAL LOAD:  22.     KG/DAY - DISPOSITION:  63.86% VIA CHEMICAL
      TRANSFORMATIONS,  27.62% BIOTRANSFORMED,   0.03% VOLATILIZED,
        8.48% EXPORTED VIA OTHER PATHWAYS.
PERSISTENCE:
 A. AT THE END OF A  180.     DAY RECOVERY PERIOD, THE WATER COLUMN HAD
      LOST  67.63% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD
      LOST  46.04% OF THEIR INITIAL BURDEN (  49.31% REMOVAL OVERALL).
 B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY 31. MONTHS.
```

Data Entry Series 1. Chemical Input Data.

AERL-ESB MODEL OF FATE OF ORGANICS IN AQUATIC ECOSYSTEMS

CHEMICAL NAME: ________________
SPFLG VECTOR (SH2, SH3+, SH4++, SH-, S): _ _ _ _ _

TABLE 1.1. SH2 (NEUTRAL MOLECULE, SPECIES #1) INPUT DATA. SPFLG(1)=1

MWT= ______ SOL = ______ VAPR= ______ HENRY= ______

KVO= ______ ESOL= ______ EVPR= ______ EHEN = ______

KPS= ______ KPB = ______ KOC = ______ KOW = ______

KAH1= ______ EAH1= ______ KNH1= ______ ENH1= ______

KAH2= ______ EAH2= ______ KNH2= ______ ENH2= ______

KAH3= ______ EAH3= ______ KNH3= ______ ENH3= ______

KBH1= ______ EBH1= ______ KOX1= ______ EOX1= ______

KBH2= ______ EBH2= ______ KOX2= ______ EOX2= ______

KBH3= ______ EBH3= ______ KOX3= ______ EOX3= ______

KBACW1= ______ QTW1= ______ KBACS1= ______ QTS1= ______

KBACW2= ______ QTW2= ______ KBACS2= ______ QTS2= ______

KBACW3= ______ QTW3= ______ KBACS3= ______ QTS3= ______

KDP= ______ RFLAT= ______ LAMAX= 0.00

QUANT1= ______ QUANT2= ______ QUANT3= ______

ABSORPTION SPECTRUM (ABS): ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

AERL-ESB MODEL OF FATE OF ORGANICS IN AQUATIC ECOSYSTEMS

CHEMICAL NAME:________________

TABLE 1.2. SH3+
(SINGLY CHARGED CATION, SPECIES #2) INPUT DATA. SPFLG(2)=1.

PKB1= ______ EPKB1= ______ SOL= ______ ESOL= ______

MWT = ______ KPS = ______ KPB= ______ KCEC= ______

KAH1= ______ EAH1= ______ KNH1= ______ ENH1= ______

KAH2= ______ EAH2= ______ KNH2= ______ ENH2= ______

KAH3= ______ EAH3= ______ KNH3= ______ ENH3= ______

KBH1= ______ EBH1= ______ KOX1= ______ EOX1= ______

KBH2= ______ EBH2= ______ KOX2= ______ EOX2= ______

KBH3= ______ EBH3= ______ KOX3= ______ EOX3= ______

KBACW1= ______ QTW1= ______ KBACS1= ______ QTS1= ______

KBACW2= ______ QTW2= ______ KBACS2= ______ QTS2= ______

KBACW3= ______ QTW3= ______ KBACS3= ______ QTS3= ______

KDP= ______ RFLAT= ______

QUANT1= ______ QUANT2= ______ QUANT3= ______

ABSORPTION SPECTRUM (ABS): ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

AERL-ESB MODEL OF FATE OF ORGANICS IN AQUATIC ECOSYSTEMS

CHEMICAL NAME:________________

TABLE 1.3. SH4++
(DOUBLY CHARGED CATION, SPECIES #3) INPUT DATA. SPFLG(3)=1.

PKB2= ______ EPKB2= ______ SOL= ______ ESOL= ______

MWT = ______ KPS = ______ KPB= ______ KCEC= ______

KAH1= ______ EAH1= ______ KNH1= ______ ENH1= ______

KAH2= ______ EAH2= ______ KNH2= ______ ENH2= ______

KAH3= ______ EAH3= ______ KNH3= ______ ENH3= ______

KBH1= ______ EBH1= ______ KOX1= ______ EOX1= ______

KBH2= ______ EBH2= ______ KOX2= ______ EOX2= ______

KBH3= ______ EBH3= ______ KOX3= ______ EOX3= ______

KBACW1= ______ QTW1= ______ KBACS1= ______ QTS1= ______

KBACW2= ______ QTW2= ______ KBACS2= ______ QTS2= ______

KBACW3= ______ QTW3= ______ KBACS3= ______ QTS3= ______

KDP= ______ RFLAT= ______

QUANT1= ______ QUANT2= ______ QUANT3= ______

ABSORPTION SPECTRUM (ABS): ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

AERL-ESB MODEL OF FATE OF ORGANICS IN AQUATIC ECOSYSTEMS

CHEMICAL NAME:______________

TABLE 1.4. SH-
(SINGLY CHARGED ANION, SPECIES #4) INPUT DATA. SPFLG(4)=1.

PKA1= ______ EPKA1= ______ SOL= ______ ESOL= ______

MWT = ______ KPS = ______ KPB= ______ KAEC= ______

KAH1= ______ EAH1= ______ KNH1= ______ ENH1= ______

KAH2= ______ EAH2= ______ KNH2= ______ ENH2= ______

KAH3= ______ EAH3= ______ KNH3= ______ ENH3= ______

KBH1= ______ EBH1= ______ KOX1= ______ EOX1= ______

KBH2= ______ EBH2= ______ KOX2= ______ EOX2= ______

KBH3= ______ EBH3= ______ KOX3= ______ EOX3= ______

KBACW1= ______ QTW1= ______ KBACS1= ______ QTS1= ______

KBACW2= ______ QTW2= ______ KBACS2= ______ QTS2= ______

KBACW3= ______ QTW3= ______ KBACS3= ______ QTS3= ______

KDP= ______ RFLAT= ______

QUANT1= ______ QUANT2= ______ QUANT3= ______

ABSORPTION SPECTRUM (ABS): ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

AERL-ESB MODEL OF FATE OF ORGANICS IN AQUATIC ECOSYSTEMS

CHEMICAL NAME:________________

TABLE 1.5. SH=
(DOUBLY CHARGED ANION, SPECIES #5) INPUT DATA. SPFLG(5)=1.

PKA2= ______ EPKA2= ______ SOL= ______ ESOL= ______

MWT = ______ KPS = ______ KPB= ______ KAEC= ______

KAH1= ______ EAH1= ______ KNH1= ______ ENH1= ______

KAH2= ______ EAH2= ______ KNH2= ______ ENH2= ______

KAH3= ______ EAH3= ______ KNH3= ______ ENH3= ______

KBH1= ______ EBH1= ______ KOX1= ______ EOX1= ______

KBH2= ______ EBH2= ______ KOX2= ______ EOX2= ______

KBH3= ______ EBH3= ______ KOX3= ______ EOX3= ______

KBACW1= ______ QTW1= ______ KBACS1= ______ QTS1= ______

KBACW2= ______ QTW2= ______ KBACS2= ______ QTS2= ______

KBACW3= ______ QTW3= ______ KBACS3= ______ QTS3= ______

KDP= ______ RFLAT= ______

QUANT1= ______ QUANT2= ______ QUANT3= ______

ABSORPTION SPECTRUM (ABS): ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

______ ______ ______ ______ ______ ______

Data Entry Series 2. Specification of Environment

Number of Compartments (KOUNT):_____________________________________

Environment Name:____

Type of compartment: 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

16 17 18 19 20 21 22 23 24 25 26 27 28 29 30

SKETCH OF ECOSYSTEM COMPARTMENTS AND INTERCONNECTIONS:

TABLE 2. INPUT DATA DESCRIBING ENVIRONMENT: GLOBAL PARAMETERS.

```
--------------------------------------------------------------------------
RAIN(MM/MO)= ______    CLOUD(10THS)= ______     LAT= ______
IRRADIANCE (WLAM,P/SQ CM/SEC/N NM):  _.___E+__   _.___E+__   _.___E+__
 _.___E+__   _.___E+__   _.___E+__   _.___E+__   _.___E+__   _.___E+__
 _.___E+__   _.___E+__   _.___E+__   _.___E+__   _.___E+__   _.___E+__
 _.___E+__   _.___E+__   _.___E+__   _.___E+__   _.___E+__   _.___E+__
 _.___E+__   _.___E+__   _.___E+__   _.___E+__   _.___E+__   _.___E+__
 _.___E+__   _.___E+__   _.___E+__   _.___E+__   _.___E+__   _.___E+__
 _.___E+__   _.___E+__   _.___E+__   _.___E+__   _.___E+__   _.___E+__
--------------------------------------------------------------------------
```

Type of compartment, "L," "E," "H," "B" (TYPEE):

Compartment No. ______

Geometry of Compartment:

SDCHR = ______

AREA = ______

STFLO = ______

NPSFL = ______

INTFL = ______

WIND = ______ *

VOL = ______

DEPTH = ______

STSED = ______

NPSED = ______

EVAP = ______ *

PCTWA = ______ **

Specifications of Compartment:

FROC = ______

AEC = ______

PH = ______

OXRAD = ______

PLRA = ______

BACTO = ______

KO2 = ______ *

DOC = ______ *

CHL = ______ *

CEC = ______

TCEL = ______

POH = ______

BIOMS = ______

BIOTM = ______

ACBAC = ______

CMPET = ______ *

DFAC = ______ *

* -- This datum for water column compartments only
** -- This datum for benthic compartments only

Type of compartment , "L," "E," "H," "B"   (TYPEE):

Compartment No. ______________

Geometry of Compartment:

SDCHR = ______
AREA = ______
STFLO = ______
NPSFL = ______
INTFL = ______
WIND = ______ *

VOL = ______
DEPTH = ______
STSED = ______
NPSED = ______
EVAP = ______ *
PCTWA = ______ **

Specifications of Compartment:

FROC = ______
AEC = ______
PH = ______
OXRAD = ______
PLRA = ______
BACTO = ______
KO2 = ______ *
DOC = ______ *
CHL = ______ *

CEC = ______
TCEL = ______
POH = ______
BIOMS = ______
BIOTM = ______
ACBAC = ______
CMPET = ______ *
DFAC = ______ *

 * -- This datum for water column compartments only
** -- This datum for benthic compartments only

TABLE 7. INPUT DATA DESCRIBING ENVIRONMENT: ADVECTIVE INTERCONNECTIONS.

COMP. NO. (JFRAD)	______	______	______	______	______
CONNECTED (ITOAD)	______	______	______	______	______
ADVECTION (ADVPR)	______	______	______	______	______
COMP. NO. (JFRAD)	______	______	______	______	______
CONNECTED (ITOAD)	______	______	______	______	______
ADVECTION (ADVPR)	______	______	______	______	______
COMP. NO. (JFRAD)	______	______	______	______	______
CONNECTED (ITOAD)	______	______	______	______	______
ADVECTION (ADVPR)	______	______	______	______	______
COMP. NO. (JFRAD)	______	______	______	______	______
CONNECTED (ITOAD)	______	______	______	______	______
ADVECTION (ADVPR)	______	______	______	______	______
COMP. NO. (JFRAD)	______	______	______	______	______
CONNECTED (ITOAD)	______	______	______	______	______
ADVECTION (ADVPR)	______	______	______	______	______
COMP. NO. (JFRAD)	______	______	______	______	______
CONNECTED (ITOAD)	______	______	______	______	______
ADVECTION (ADVPR)	______	______	______	______	______
COMP. NO. (JFRAD)	______	______	______	______	______
CONNECTED (ITOAD)	______	______	______	______	______
ADVECTION (ADVPR)	______	______	______	______	______
COMP. NO. (JFRAD)	______	______	______	______	______
CONNECTED (ITOAD)	______	______	______	______	______
ADVECTION (ADVPR)	______	______	______	______	______
COMP. NO. (JFRAD)	______	______	______	______	______
CONNECTED (ITOAD)	______	______	______	______	______
ADVECTION (ADVPR)	______	______	______	______	______
COMP. NO. (JFRAD)	______	______	______	______	______
CONNECTED (ITOAD)	______	______	______	______	______
ADVECTION (ADVPR)	______	______	______	______	______
COMP. NO. (JFRAD)	______	______	______	______	______
CONNECTED (ITOAD)	______	______	______	______	______
ADVECTION (ADVPR)	______	______	______	______	______
COMP. NO. (JFRAD)	______	______	______	______	______
CONNECTED (ITOAD)	______	______	______	______	______
ADVECTION (ADVPR)	______	______	______	______	______

TABLE 8. INPUT DATA DESCRIBING ENVIRONMENT: TURBULENT INTERCONNECTIONS.

COMP. NO. (JTURB) ------ ------ ------ ------ ------
CONNECTED (ITURB) ------ ------ ------ ------ ------
X-SECTION (XSTUR) ------ ------ ------ ------ ------
CHAR. LN. (CHARL) ------ ------ ------ ------ ------
EDDY DISP. (DSP) ------ ------ ------ ------ ------

COMP. NO. (JTURB) ------ ------ ------ ------ ------
CONNECTED (ITURB) ------ ------ ------ ------ ------
X-SECTION (XSTUR) ------ ------ ------ ------ ------
CHAR. LN. (CHARL) ------ ------ ------ ------ ------
EDDY DISP. (DSP) ------ ------ ------ ------ ------

COMP. NO. (JTURB) ------ ------ ------ ------ ------
CONNECTED (ITURB) ------ ------ ------ ------ ------
X-SECTION (XSTUR) ------ ------ ------ ------ ------
CHAR. LN. (CHARL) ------ ------ ------ ------ ------
EDDY DISP. (DSP) ------ ------ ------ ------ ------

COMP. NO. (JTURB) ------ ------ ------ ------ ------
CONNECTED (ITURB) ------ ------ ------ ------ ------
X-SECTION (XSTUR) ------ ------ ------ ------ ------
CHAR. LN. (CHARL) ------ ------ ------ ------ ------
EDDY DISP. (DSP) ------ ------ ------ ------ ------

COMP. NO. (JTURB) ------ ------ ------ ------ ------
CONNECTED (ITURB) ------ ------ ------ ------ ------
X-SECTION (XSTUR) ------ ------ ------ ------ ------
CHAR. LN. (CHARL) ------ ------ ------ ------ ------
EDDY DISP. (DSP) ------ ------ ------ ------ ------

COMP. NO. (JTURB) ------ ------ ------ ------ ------
CONNECTED (ITURB) ------ ------ ------ ------ ------
X-SECTION (XSTUR) ------ ------ ------ ------ ------
CHAR. LN. (CHARL) ------ ------ ------ ------ ------
EDDY DISP. (DSP) ------ ------ ------ ------ ------

COMP. NO. (JTURB) ------ ------ ------ ------ ------
CONNECTED (ITURB) ------ ------ ------ ------ ------
X-SECTION (XSTUR) ------ ------ ------ ------ ------
CHAR. LN. (CHARL) ------ ------ ------ ------ ------
EDDY DISP. (DSP) ------ ------ ------ ------ ------

COMP. NO. (JTURB) ------ ------ ------ ------ ------
CONNECTED (ITURB) ------ ------ ------ ------ ------
X-SECTION (XSTUR) ------ ------ ------ ------ ------
CHAR. LN. (CHARL) ------ ------ ------ ------ ------
EDDY DISP. (DSP) ------ ------ ------ ------ ------

Data Entry Series 3. Chemical Loadings.

Chemical Name --

Environment Name: ------------------------------------

Number of Compartments (KOUNT): -----

Type of Compartment (TYPEE): 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

16 17 18 19 20 21 22 23 24 25 26 27 28 29 30

TABLE 12. TOXICANT LOADINGS (KG/HR) BY SYSTEM ELEMENT.

ELEMENT	STREAM FLOW (STRLD)	RAINFALL (PCPLD)	INTERFLOW (IFLLD)	NPS LOAD (NPSLD)	DRIFT LOAD (DRFLD)
1	----------	----------	----------	----------	----------
2	----------	----------	----------	----------	----------
3	----------	----------	----------	----------	----------
4	----------	----------	----------	----------	----------
5	----------	----------	----------	----------	----------
6	----------	----------	----------	----------	----------
7	----------	----------	----------	----------	----------
8	----------	----------	----------	----------	----------
9	----------	----------	----------	----------	----------
10	----------	----------	----------	----------	----------
11	----------	----------	----------	----------	----------
12	----------	----------	----------	----------	----------
13	----------	----------	----------	----------	----------
14	----------	----------	----------	----------	----------
15	----------	----------	----------	----------	----------
16	----------	----------	----------	----------	----------
17	----------	----------	----------	----------	----------
18	----------	----------	----------	----------	----------
19	----------	----------	----------	----------	----------
20	----------	----------	----------	----------	----------
21	----------	----------	----------	----------	----------
22	----------	----------	----------	----------	----------
23	----------	----------	----------	----------	----------
24	----------	----------	----------	----------	----------
25	----------	----------	----------	----------	----------
26	----------	----------	----------	----------	----------
27	----------	----------	----------	----------	----------
28	----------	----------	----------	----------	----------
29	----------	----------	----------	----------	----------
30	----------	----------	----------	----------	----------

3.2 Interactive System Commands and Keywords.

This Section describes the functioning of EXAMS' interactive commands and the response options for the commands. The text is also available to an interactive user via the HELP command.

BASE (i.e., EXAMS' response to a simple EXAMS > HELP)

EXAMS is an interactive computer language and modeling system for analyzing exposure, fate, distribution, and persistence of synthetic organic chemicals in aquatic ecosystems. The EXAMS command language allows a user to select chemicals (COMPOUND and RECALL commands) and ecosystems (ENVIRONMENT and RECALL) from external data bases, specify (CHANGE) the chemical loadings on the system, conduct an exposure analysis (RUN), retrieve the results (LIST, PLOT, PRINT), modify (CHANGE) any of the input data and reRUN the system, and STORE new data for later RECALL.

When entering commands and response options, any EXAMS vocabulary word can be abbreviated to the characters needed for EXAMS to decode the word. For example, a RUN command can be entered as RUN or as RU. To get HELP for a particular keyword, type HELP <keyword>. HELP is available for the name of any input VARIABLE, and for the keywords:

```
ADVECTION   AUDIT       CHANGE    CHEMISTRY   COMPOUND    DESCRIBE
ENVIRONMENT ERASE       EXIT      GEOMETRY    GLOBALS     HELP
LIST        LOADS       PLOT      POINT       PRINT       PROFIL
QUALITY     QUIT        RECALL    RUN         SHOW        STORE
STOP        TURBULENCE
```

ADVECTION

The ADVECTION option of the SHOW command returns the input data characterizing the advective interconnections among compartments of the current ecosystem. Up to NCON interconnections can be specified; inactive pathways are not displayed. Syntax is

```
EXAMS > SHOW ADVECTION
```

The index vectors contain the source (JFRAD, J FRom ADvection) and receiving (ITOAD, I TO ADvection) compartments in homologous locations. Parameter ADVPR gives the proportion of the total advective flow through compartment JFRAD that leaves via the

(ITOAD,JFRAD) pathway.

Advective interconnections can be re-specified (CHANGEd) at will. Export pathways are designated by loading a "0" in ITOAD. Should the new definition fail to adhere to the principle of conservation of mass, however, EXAMS will decline to RUN the simulation.

AUDIT

The AUDIT command makes a record of all subsequent commands entered into EXAMS. The syntax of the command is:

```
EXAMS > AUDIT
```

After receiving an AUDIT command, EXAMS copies each following user command and/or response to the output data file defined by FORTRAN logical unit AUDOUT. After leaving EXAMS >, this file can be retrieved and used as a record of the session.

CHANGE

The CHANGE command alters the value of any input datum. The syntax of this command is

```
EXAMS > CHANGE <aaa> TO <nnn>
```

where <aaa> is the name of the variable and <nnn> is its new value. EXAMS variables may be scalars, vectors, or matrices. (The meaning of the vector and matrix indices (subscripts) is explained under <HELP VARIABLES>. For example, the command

```
EXAMS > CHANGE PH(4) TO 7.6
```

would alter the pH of compartment 4 to 7.60. EXAMS also allows the use of "wild cards" <*> for vector and matrix indices. For example, the command

```
EXAMS > CHANGE PH(*) TO 7.6
```

alters the pH of ALL compartments to 7.60. In using the CHANGE command, it is important that matrix indices be specified in the proper (row, column) order. For example, CHANGEing ENH(3,1) is not equivalent to CHANGEing ENH(1,3): the former refers to the biosorbed form of a neutral molecule (SH2); the latter to the dissolved form of an SH4++ cation! The outcome of a CHANGE can always be checked by invoking the appropriate SHOW option.

CHEMISTRY

The CHEMISTRY option of the SHOW command returns the chemical data currently available to EXAMS for simulation RUNs. Syntax is:

```
EXAMS > SHOW CHEMISTRY
```

For convenience, all MATRIX variables include the row index of the datum as a suffix; the column index (chemical SPECIES #) is given in the table header. The latter quantity is also the proper index for VECTOR variables. Thus for example, a reference to KBACW3 in the chemical data for SPECIES #1 gives the value for KBACW(3,1), the 2nd-order rate constant for biolysis of the biosorbed form of a neutral (SH2) molecule in the water column. This datum can be altered by:

```
EXAMS > CHANGE KBACW(3,1) TO <new number>
```

All input data can be CHANGEd; the DESCRIBE and HELP commands can be used to ascertain the dimensions and attributes of the input variables.

COMPOUND

COMPOUND is used as a stand-alone command AND as a keyword in the SHOW, STORE, RECALL, and ERASE commands. (Type <HELP SHOW>, <HELP STORE>, etc. for a description of these useages.) The stand-alone COMPOUND command has two distinct functions: it can be used either to SELECT a chemical from the fixed data base, or to reNAME the current chemical. The syntax for the SELECT option is:

```
EXAMS > COMPOUND IS <aaa>
```

where "aaa" is the abbreviation of an available chemical. (Type <SHOW COMPOUNDS> for a table of contents.) The syntax for the NAME option is:

```
EXAMS > COMPOUND NAME IS <bbb>
```

after which "bbb" (up to 60 characters permitted) will be entered as part of the title for all output tables produced by EXAMS. For example, the command:

```
     EXAMS > COMPOUND IS DBC
```

loads the data base describing 7H-dibenzo[c,g]carbazole, a (carcinogenic) nitrogen heteroclycic compound found in energy-related effluents. The command:

```
EXAMS > COMPOUND NAME IS <7H-dibenzo[c,g]carbazole with high biolysis>
```

would result in the text <7H- ... > being printed as part of the title of EXAMS' subsequent outputs.

DESCRIBE

The DESCRIBE command returns the attributes of a specific input datum. Command syntax is

```
              EXAMS > DESCRIBE <nnn>
```

where <nnn> is the name of an input variable.

```
For example,  EXAMS > DESCRIBE WLAMG

    returns:  WLAM is a REAL VECTOR with 39 rows.

Or:           EXAMS > DES ENH

    returns:  ENH is a REAL MATRIX with 3 rows and 5 columns.
```

The information returned by DESCRIBE is needed when SHOWing or CHANGEing an input datum.

ERASE

The ERASE command clears a selected location if the user chemical or environmental data base (UDBs). The syntax of the command is:

```
        EXAMS > ERASE COMPOUND #
or
        EXAMS > ERASE ENVIRONMENT #
```

where "#" is the location in the UDB to be cleared. This command can be used to help protect the confidentiality of chemical or environmental data.

ENVIRONMENT

ENVIRONMENT is used as a stand-alone command AND as a keyword in the SHOW, STORE, RECALL, and ERASE commands. (Type <HELP SHOW>, etc. for a description of the latter useages.) The stand-alone ENVIRONMENT command has two distinct functions. It is used either to SELECT an ecosystem from the fixed data file, or to reNAME the current system. The syntax for the SELECT option is

```
EXAMS > ENVIRONMENT IS <aaa>
```

where "aaa" is the name of an available ecosystem. Type <SHOW ENVIRONMENTS> for a table of contents. The syntax for the NAME option is

```
EXAMS > ENVIRONMENT NAME IS <bbb>
```

after which "bbb" (up to 60 characters permitted) will be used as part of the title for all of EXAMS' subsequent ouput tables. For example, the command:

```
EXAMS > ENVIRONMENT IS POND
```

loads the fixed data base describing a pond ecosystem. The command:

```
EXAMS > ENVIRONMENT NAME IS <Southeastern Pond with pH of 6>
```

would result in the text <Sou ... > being printed as part of the title of EXAMS' subsequent outputs.

EXIT

The EXIT command is used to terminate use of EXAMS and return to the operating system, e.g., PDS>. The syntax of the command is

```
EXAMS > EXIT
```

The EXIT command is also used to abort a command sequence when the command has been inadvertantly initiated. For example, given the input

```
EXAMS > COMPOUND <CR>,    EXAMS will return the prompt:
```

```
SELECT or NAME a compound or EXIT >
```

Responding to this prompt with <EXIT> will return you to the EXAMS > prompt with no action taken on the COMPOUND command.

GEOMETRY

The GEOMETRY option of the SHOW command returns a compartment-by- compartment listing of environmental data describing the current ecosystem. The compartment number given with each block of data is the appropriate vector index for CHANGEing the variables listed in the block. The attributes and dimensions of each parameter can be inspected via the DESCRIBE and HELP commands. Command syntax is

```
EXAMS > SHOW GEOMETRY
```

GLOBALS

The GLOBALS option of the SHOW command returns the values of global (i.e., not specific to any single compartment) environmental descriptors. The attributes and dimensions of each parameter can be accessed via DESCRIBE and HELP. CLOUD, LAT, and WLAM are used to calulate photolysis rates of the chemical; RAIN is part of the input hydrologic data. Each input datum can be CHANGEd to any desired value.

HELP

The HELP command is used to obtain information about the use of EXAMS vocabulary words (commands and response options) and to obtain definitions and physical dimensions of the chemical and environmental input data. Input data can be CHANGEd from the nominal values held in the data bases to any desired number. Syntax of the HELP command is:

```
EXAMS > HELP <KEYWORD>
```

where <KEYWORD> can be the name of a command (e.g., SHOW), an optional response word (e.g., ADVECTION), or the name of an input variable (e.g., KBACW). For example, typing

```
EXAMS > HELP HELP
```

invoked this message.

The structure of the input data is described under the <keyword> VARIABLES, but VARIABLES is not a part of the formal EXAMS vocabulary.

LIST

The LIST command issues reports (based on simulation studies) that describe the exposure, distribution, fate, and persistence of a chemical in a particular ecosystem/load situation. The reports include the input data describing the chemical and the ecosystem, fate and exposure data at steady-state, pseudo-first-order half-lives by process, and a system self-cleansing time based on all processes acting in concert. The command sytax is

```
EXAMS > LIST <#>
```

where "#" can be any of the integers {1,2,3, ..., 17} or "ALL". Alternatively, issuing the command

```
EXAMS > LIST <CR>
```

generates the EXAMS prompt

```
Table >
```

Typing <HELP> (rather than <#>) in response to "Table >" will elicit a numerical listing and description of the available output tables.

LOADS

The LOADS option of the SHOW command returns a tabulation of the chemical loadings on the ecosystem. The first column of this table gives the number of the compartment receiving the load; these numbers are the appropriate vector indices for entering or CHANGEing loads. Command syntax is:

```
EXAMS > SHOW LOADS
```

The internal variable names (used for CHANGE) for each type of load listed in the columns of the <SHOW LOADS> tabulation are:

STREAM FLOW --- STRLD
RAINFALL --- PCPLD
INTERFLOW --- IFLLD

NPS LOAD --- NPSLD
DRIFT LOAD --- DRFLD

Each time a new COMPOUND or ENVIRONMENT is selected, all chemical loads are reset to zero. If a given loading is found (during a simulation RUN) to violate assumptions of the model (e.g., by supersaturating an inlet carrier flow), or is found to be inappropriate (e.g., a PCPLD to a (B)enthic compartment), that load is modified as necessary. These new loadings are stored in the LOADS matrix and returned to the user, i.e. the erroneous loadings are discarded and the new values are retained.

PLOT

The PLOT command produces a graphic display of selected results from the most recent simulation. PLOT contains 3 levels of subcommands:

(1) - the type of PLOT desired -- <POINT> or <PROFIL>

(2) - the concentration variable -- <TOTAL>, <DISSOLVED>, <PARTICULATE>, <BIOTA>, or <MASS>

(3a) - the "statistical" variable -- <AVE,MAX,MIN,MINMAX> (under POINT)

(3b) - the environmental zone -- <WATER,SEDIMENTS> (under PROFIL)

PLOT requires that each of these options be specified in the order given above. An example of the syntax of this command is

```
EXAMS > PLOT <CR>

Enter POINT, PROFIL, HELP or EXIT > <POINT>

Enter TOTAL, DISSOLVED, PARTICULATE, BIOTA, MASS, HELP or EXIT > <TOTAL>

Enter AVE, MAX, MIN, MINMAX, HELP, or EXIT > <AVE>
```

The HELP option produces a definition of each of the available options; the EXIT option will abort PLOT and return to the EXAMS > prompt.

The PLOT command can also be executed via a single line, i.e., the PLOT requested in the example given above could also be entered as:

```
EXAMS > <PL PO TO AV> <CR>
```

(Remember that you need enter only enough letters of any EXAMS word to make it distinct.)

POINT

POINT is a type of PLOT (c.f.) available through EXAMS graphics. Specifically, the <POINT> response to:

```
     EXAMS > PLOT <CR>

     Enter POINT, PROFIL, HELP, or EXIT > <POINT>
```

produces a vertical profile of chemical concentration in the ecosystem. EXAMS then requires that a concentration variable (TOTAL, DISSOLVED, PARTICULATE, BIOTA, or MASS) and a "statistical" variable (AVE, MAX, MIN, or MINMAX) be specified. Plots of maximum and minimum values include the compartment number where that concentration occurs.

The concentration (TOTAL, DISSOLVED, PARTICULATE, BIOTA, MASS) and "statistical" (AVE, MAX, MIN, MINMAX) variables are defined in the internal HELP responses of the PLOT command.

PRINT

The print command performs the same function as the LIST command, but the output is routed to a line printer. Syntax is

```
                 EXAMS > PRINT <integer>
```

where <integer> is any of the numbered output tables (1 through 17). The command <PRINT ALL> routes all 17 tables to the printer.

PROFIL

PROFIL is a type of PLOT (c.f.) available through EXAMS graphics. Specifically, the <PROFIL> response to:

```
EXAMS > PLOT <CR>

Enter POINT, PROFIL, HELP, or EXIT > <PROFIL>
```

produces a longitudinal PROFILe of chemical concentrations in the ecosystem. EXAMS then requires that a concentration variable (TOTAL, DISSOLVED, PARTICULATE, BIOTA, or MASS) and an environmental zone (WATER or SEDIMENTS) be specified. The abscissa of the resulting PLOT is organized according to downstream progression in the ecosystem (i.e., by ascending compartment number). In the case of ecosystems that are vertically inhomogeneous, the PLOT will show separate entries for, e.g., the epilimnion and hypolimnion. These can be distinguished by noting the compartment number and letter codes given on the plots (e.g., E for epilimnion and H for hypolimnion).

The concentration variables (TOTAL, DISSOLVED, PARTICULATE, BIOTA, MASS) and environmental zones (WATER, SEDIMENT) are defined in the internal HELP responses of the PLOT command.

QUALITY

The QUALITY option of the SHOW command returns a compartment-by- compartment listing of canonical water quality data describing the current ecosystem. The compartment number given with each block of data is the appropriate vector index for CHANGEing the variables listed in the block. The attributes and dimensions of each parameter can be inspected via the DESCRIBE and HELP commands. Command syntax is

```
EXAMS > SHOW QUALITY
```

QUIT

The QUIT command is used to terminate use of EXAMS and return to the operating system, e.g., PDS>. The syntax of the command is

```
EXAMS > QUIT
```

RECALL

The RECALL command retrieves chemical or environmental data from the user data bases (UDBs) for use in EXAMS. Command syntax is:

```
        EXAMS > RECALL COMPOUND #
or
        EXAMS > RECALL ENVIRONMENT #
```

where "#" is the location of the data in the UDB. The table of contents of the UDBs can be generated via a SHOW command, that is,

```
        EXAMS > SHOW USER COMPOUNDS
or
        EXAMS > SHOW USER ENVIRONMENTS
```

RUN

The RUN command instructs EXAMS to execute a simulation and create the output tables describing the results.

Command syntax is `EXAMS > RUN <CR>`

where <CR> is a carriage return. Simulation RUNs cannot be executed until a COMPOUND and an ENVIRONMENT have been selected, and at least one non-zero LOAD has been specified. If any of these steps has not been completed when the RUN command is issued, EXAMS prints a reminder and aborts the RUN.

SELECT

SELECT is not an EXAMS user keyword. EXAMS uses SELECT as a prompt when a COMPOUND or ENVIRONMENT command is issued without a complete command sequence. For example,

```
                EXAMS > COMPOUND <CR>
elicits
                SELECT or NAME a compound or EXIT >
```

EXAMS will now recognize either <SELECT> or <NAME> and prompt for the remaining input. For example, to retrieve PCR from the fixed chemical data base:

```
                SELECT or NAME a compound or EXIT > <SELECT>

                Select a compound > <PCR>

                Compound selected > p-Cresol
```

SHOW

The SHOW command is used to extract and display information describing the current data available to EXAMS. Command syntax is:

```
EXAMS > SHOW <keyword>     where "keyword" can be:
```

ADVECTION, CHEMISTRY, COMPOUND, ENVIRONMENT, GEOMETRY, GLOBALS LOADS, QUALITY, TURBULENCE, USER, or <a VARIABLE name>

For example,   EXAMS > <SHOW COMPOUND> or <SHOW USER COMPOUNDS>

generate tables of contents of the chemical data bases.

Similarly,

EXAMS > <SHOW ENVIRONMENT> or <SHOW USER ENVIR>

generate tables of contents of the canonical environment files.

Having selected a particular chemical and/or ecosystem, SHOW can be coupled to the above <keywords> to inspect the available data. Type <HELP <keyword>> for a discussion of the data accessed by each keyword. The SHOW command can also be used to display the current numerical value of any CHANGEable input datum. Type <HELP VARIABLES> for an explanation of this use of the SHOW command.

STOP

The STOP command is used to terminate use of EXAMS and return to the operating system, e.g., PDS>. The syntax of the command is

```
EXAMS > STOP
```

STORE

The STORE command moves EXAMS' current chemical or environmental data into a user data base (UDB). Command syntax is:

```
EXAMS > STORE COMPOUND #
```

or

```
EXAMS > STORE ENVIRONMENT #
```

where "#" is an available location in the UDB. If the selected location in the UDB is already in use, EXAMS will report the fact and require confirmation that the existing data are to be overwritten and destroyed.

TERMINAL

The TERMINAL command identifies your terminal for EXAMS' plotting routines. The syntax of the command is:

```
EXAMS > TERMINAL IS <options>
```

The available options are: (1) <VT55> -- a DEC terminal equipped for graphics, (2) <4010> -- any Tectronix series (4010, 4012, 4014, etc.) with graphics capability, and (3) <TTY> for all other alphanumeric terminals lacking an internal graphics package. EXAMS should have this information prior to initiation of the PLOT command. If it does not, EXAMS will execute a TTY plot.

TURBULENCE

The TURBULENCE option of the SHOW command returns the input data characterizing the dispersive interconnections among compartments of the current ecosystem. Up to NCON interconnections can be specified; inactive pathways are not displayed. Syntax is

```
EXAMS > SHOW TURBULENCE
```

Homologous pairs in the index vectors (JTURB, ITURB) serve to define the system exchange pathways (a "0" in either vector, paired with a non-zero compartment number in the homologue, defines a boundary condition). XSTUR is the crossectional area for pathway (JTURB, ITURB); CHARL is its characteristic length (mean of mixing lengths or compartment dimensions along the flow path); DSP is the eddy dispersion coefficient.

Dispersive interconnections can be re-specified (CHANGEd) as desired. If the new definition includes non-existent compartments (e.g., a JTURB .GT. KOUNT) or compartments not connected to the main system, however, EXAMS may in some cases decline to RUN simulations.

USER

USER is a subpart of the SHOW command. USER directs EXAMS to the chemical and environmental user data bases (UDBs). The commands:

```
        EXAMS > SHOW USER COMPOUNDS
```

and

```
        EXAMS > SHOW USER ENVIRONMENTS
```

generate tables of contents for these UDBs.

VARIABLES

The chemical and environmental data used for EXAMS' computations are continually available for inspection and alteration by the interactive user. The data can be inspected in tabular form (type <HELP SHOW> for a description), or the current value of any single datum can be SHOWn. For example,

```
    EXAMS > SHOW PH(4)
```

will return:

```
    PH IS 7.000
```

when the pH of compartment number 4 is 7.0. A description of each block of data (ADVECTION, CHEMISTRY, GEOMETRY, GLOBALS, LOADS, QUALITY, TURBULENCE) is given under <HELP <KEYWORD>> where <KEYWORD> is the name of one of these blocks. Typing <HELP <nnn>> where <nnn> is the name of an input datum will elicit a definition of the variable (e.g., <HELP PH>); also see <DESCRIBE>. When CHANGEing or SHOWing a variable, the vector/matrix indices must be entered in the proper (row, column) order (because <nnn(1,3)> is by no means equivalent to <nnn(3,1)>). In a system that can handle 10-compartment ecosystems, the dimensions of variables include the values: (5), (3,5), (10), (30), (5,39), and (39). Dimension (5) refers to the ionic species of the chemical (c.f. <HELP SPFL>); dimension (3) refers to physical forms (1: dissolved, 2: sediment-sorbed, 3: biosorbed); dimension (3,5) to matrices of molecular configurations amalgamating (3) and (5) (e.g., <nnn(3,1)> refers to a biosorbed neutral molecule); dimension (10) to ecosystem compartments; dimension (30) to compartment interconnections; and dimension (39) refers to irradiance and light absorption intervals (see Table 2.18).

3.3 Tutorial Interactive Sessions

This Section contains four sample EXAMS sessions designed to introduce the user to the EXAMS facility. Although each session has underlying pedagogical objectives, the nominal user objectives are:

3.3.1. To enter the EXAMS system, execute runs of a selected chemical in selected ecosystems, secure selected plots and output listings of the results, and terminate the session.

3.3.2. To analyze the persistence of a new chemical in a particular ecosystem, given meager input data.

3.3.3. To execute a sensitivity analysis defining the need for accuracy in rate constants for a particular chemical/environment situation.

3.3.4. To enter a new set of chemical and environmental data, evaluate the behavior of the chemical, and store the data in the UDBs.

The on-line help file can be used as a reminder of the syntax of any command; its use is illustrated in Session 1. Once a command has been invoked, in general a carriage return <CR> will cause EXAMS to return a prompt that includes a listing of the available response options.

EXAMS' interactive capabilites can be used to enter both chemical and environmental data. New chemicals and new environments can be specified (via the CHANGE command), given distinctive names up to 60 characters long (NAME command), and stored in user data bases (STORE command, either as STORE COMPOUND or STORE ENVIRONMENT). The User Data Bases can be inspected via <SHOW USER COMPOUNDS> and <SHOW USER ENVIRONMENTS>, which elicit a table of the current contents.

When entering new chemical data, the UNS (unspecified) compound is available as a template. UNS is a neutral compound, but the template can be expanded by CHANGEs to the SPFLG vector (see Glossary). Similarly, the UNS environment serves as a template for entering new environmental data. In this case, UNS has but a single compartment. The first step in entering a new ecosystem is therefore to CHANGE parameter KOUNT to the desired number of compartments, followed by a specification of the TYPEE of each sector of the system.

Environmental and chemical data in the User Data Bases are permanently stored and can be retrieved for use in subsequent sessions via the RECALL command. Unlike the COMPOUND command, RECALL takes a numerical location for its data retrieval. For example,

```
EXAMS > RECALL ENV 34
```

loads data at position 34 in the data base into current memory.

3.3.1 Tutorial Session #1: Basic Familarity with EXAMS

Objectives: basic familiarity with EXAMS, use of command statements (SHOW, COMPOUND, ENVIRONMENT, RUN, HELP, CHANGE, LIST, PLOT) and response options (CHEMISTRY, LOADS, POINT, PROFIL, etc.).

```
PDS> RUN EXAMS
17:37:59
          Welcome to EXAMS
   EXposure Analysis Modeling System
Athens Environmental Research Laboratory
    Released for field trials Jan-81


The ATHENS collection of compounds is available for your use.


EXAMS > SHOW COMPOUNDS


    CHEMICAL NAME                         COMMON NAME

  1 UNSPECIFIED CHEMICAL                   UNS
  2 9H-CARBAZOLE                           CAR
  3 BENZO[f]QUINOLINE                      BFQ
  4 7H-DIBENZO[c,g]CARBAZOLE               DBC
  5 BENZO[b]THIOPHENE                      BT
  6 DIBENZOTHIOPHENE                       DBT
  7 BENZ[a]ANTHRACENE                      BA
  8 p-CRESOL                               PCR
  9 BENZO[a]PYRENE                         BAP
 10 MIREX                                  MIR
 11 METHYL PARATHION                       MP
 12 QUINOLINE                              QUI

EXAMS > COMPOUND IS PCR

Compound selected > p-CRESOL

EXAMS > SHOW CHEMISTRY
Compound characteristics for > p-CRESOL

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: p-CRESOL
ECOSYSTEM: Unspecified Environment
```

```
----------------------------------------------------------------------
TABLE 1.1.  SH2 (NEUTRAL MOLECULE, SPECIES  1) INPUT DATA.
MWT=  108.1      SOL =  1800.      VAPR= 0.1080      HENRY= 0.0000
KVO= 1.2000E-03 ESOL= 0.0000      EVPR= 0.0000      EHEN = 0.0000
KPS=  10.00      KPB =  20.00      KOC = 0.0000      KOW  = 0.0000
KAH1= 0.0000      EAH1= 0.0000      KNH1= 0.0000      ENH1= 0.0000
KAH2= 0.0000      EAH2= 0.0000      KNH2= 0.0000      ENH2= 0.0000
KAH3= 0.0000      EAH3= 0.0000      KNH3= 0.0000      ENH3= 0.0000
KBH1= 0.0000      EBH1= 0.0000      KOX1=  12.57      EOX1=  10.00
KBH2= 0.0000      EBH2= 0.0000      KOX2= 0.0000      EOX2= 0.0000
KBH3= 0.0000      EBH3= 0.0000      KOX3= 0.0000      EOX3= 0.0000
KBACW1= 5.2000E-07 QTW1=  2.000      KBACS1= 5.2000E-07 QTS1=  2.000
KBACW2= 0.0000     QTW2= 0.0000      KBACS2= 0.0000     QTS2= 0.0000
KBACW3= 0.0000     QTW3= 0.0000      KBACS3= 0.0000     QTS3= 0.0000
KDP= 0.0000     RFLAT=  40.00     LAMAX=     0.00
QUANT1= 7.9000E-02 QUANT2= 0.0000     QUANT3= 0.0000
ABSORPTION SPECTRUM (ABS):    14.00        3.800        2.400
  2.000       0.0000       0.0000       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
WOULD YOU LIKE INFORMATION FOR SH- ?
ENTER Y, N, OR Q TO QUIT > Y

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: p-CRESOL
ECOSYSTEM: Unspecified Environment
----------------------------------------------------------------------
TABLE 1.4.  SH- (SINGLY CHARGED ANION, SPECIES  4) INPUT DATA.
PKA1=  10.20      EPKA1= 0.0000      SOL= 1.8000E+04  ESOL= 0.0000
MWT =  108.1      KPS =  50.00       KPB=  10.00      KAEC= 0.0000
KAH1= 0.0000      EAH1= 0.0000      KNH1= 0.0000      ENH1= 0.0000
KAH2= 0.0000      EAH2= 0.0000      KNH2= 0.0000      ENH2= 0.0000
KAH3= 0.0000      EAH3= 0.0000      KNH3= 0.0000      ENH3= 0.0000
KBH1= 0.0000      EBH1= 0.0000      KOX1=  12.57      EOX1=  10.00
KBH2= 0.0000      EBH2= 0.0000      KOX2= 0.0000      EOX2= 0.0000
KBH3= 0.0000      EBH3= 0.0000      KOX3= 0.0000      EOX3= 0.0000
KBACW1= 5.2000E-07 QTW1=  2.000      KBACS1= 5.2000E-07 QTS1=  2.000
KBACW2= 0.0000     QTW2= 0.0000      KBACS2= 0.0000     QTS2= 0.0000
KBACW3= 0.0000     QTW3= 0.0000      KBACS3= 0.0000     QTS3= 0.0000
KDP= 0.0000     RFLAT=  40.00
QUANT1= 7.9000E-02 QUANT2= 0.0000     QUANT3= 0.0000
ABSORPTION SPECTRUM (ABS):    3748.        3537.        3100.
  2575.        1933.        1310.        840.0        505.0        272.0
  130.0        80.00       0.0000       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
 0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
```

```
EXAMS > SHO ENVIRON
   1 UNSPECIFIED ENVIRONMENT
   2 POND
   3 OLIGOTROPHIC LAKE
   4 EUTROPHIC LAKE
   5 RIVER

EXAMS > EMV IS OLIGOTROPHIC LAKE
Command not recognized. Enter help for command info.

EXAMS > ENV IS OLIG

Selected environment is: OLIGOTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST
DEFINITION

EXAMS > RUN

No load specified.

Simulation not performed.


EXAMS > HELP LOAD
The LOADS option of the SHOW command returns a tabulation of the
chemical loadings on the ecosystem.  The first column of this table
gives the number of the compartment receiving the load; these numbers
are the appropriate vector indices for entering or CHANGEing loads.
Command syntax is
                        EXAMS > SHOW LOADS
The internal variable names (used for CHANGE) for each type of load
listed in the columns of the <SHOW LOADS> tabulation are:

                STREAM FLOW    ---    STRLD
                RAINFALL       ---    PCPLD
                INTERFLOW      ---    IFLLD
                NPS LOAD       ---    NPSLD
                DRIFT LOAD     ---    DRFLD

Each time a new COMPOUND or ENVIRONMENT is selected, all chemical loads
are reset to zero.  If a given loading is found (during a simulation
RUN) to violate assumptions of the model (e.g. by supersaturating an
inlet carrier flow), or is found to be inappropriate (e.g. a PCPLD to a
(B)enthic compartment), that load is modified as necessary.  These new
loadings are stored in the LOADS matrix and returned to the user, i.e.
the erroneous loadings are discarded and the new values are retained.

EXAMS > CHANGE STRLD(1) TO 0.5

EXAMS > CH NPSLD(6) TO .05
EXAMS > SHOW LOADS
Environment: OLIGOTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
Compartments (KOUNT):  7
                              1  2  3  4  5  6  7
Type of compartment (TYPEE):  L  B  E  H  B  L  B
TABLE 12.  TOXICANT LOADINGS (KG/HR) BY SYSTEM ELEMENT.
------------------------------------------------------------------------
ELEMENT  STREAM FLOW    RAINFALL    INTERFLOW     NPS LOAD    DRIFT LOAD
-------  -----------   ----------   ----------   ----------   ----------
   1      0.5000
   2
   3
   4
   5
   6                                             5.0000E-02
   7
------------------------------------------------------------------------


EXAMS > RUN

Simulation beginning for:
Compound: p-CRESOL
Environment: OLIGOTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
with a load of (kg/hr) >  0.5500000

Run complete.

EXAMS > LIST

 Table > HELP
  1 Input chemistry
  2 Input data describing environment: GLOBAL parameters
  3 Input data describing environment: BIOLOGICAL parameters
  4 Input data describing environment: DEPTH and INFLOWS
  5 Input data describing environment: SEDIMENTS characteristics
  6 Input data describing environment: AERATION, LIGHT, MISC.
  7 Input data describing environment: ADVECTIVE INTERCONNECTIONS
  8 Input data describing environment: TURBULENT INTERCONNECTIONS
  9 Transport profile of ecosystem
 10 Kinetic profile of organic toxicant
 11 Canonical profile of ecosystem
 12 Toxicant loadings
 13 Distribution of toxicant at steady-state
 14 Average, maxima  and minima at steady-state
 15 Analysis of fate of toxicant
 16 Post-load decay kinetics
 17 Exposure analysis summary
ALL ENTIRE REPORT


 Table > 15
```

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: p-CRESOL
ECOSYSTEM: OLIGOTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
----------------------------------------------------------------------
TABLE 15.  ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.
----------------------------------------------------------------------
            PROCESS                 MASS FLUX    % OF LOAD    HALF-LIFE*
                                     KG/DAY                      DAYS
      ----------------------        ---------    ---------    ---------
      HYDROLYSIS                    0.0000         0.00          ---
      OXIDATION                      2.944        22.30         442.6
      PHOTOLYSIS                    0.3858         2.92         3378.
  ALL CHEMICAL PROCESSES             3.330        25.22         391.3
----------------------------------------------------------------------
      WATER COLUMN (BACTERIA)        1.660        12.57         776.2
      BOTTOM SEDIMENTS (BACTERIA)   2.0953E-03     0.02         7155.
  TOTAL BIOLYSIS                     1.662        12.59         784.2
----------------------------------------------------------------------
      VOLATILIZATION                0.2547         1.93         5115.
      WATER-BORNE EXPORT             7.954        60.26         163.8
----------------------------------------------------------------------
TRANSFORMATION AND TRANSPORT         13.20       100.00
TOTAL SYSTEM LOAD                    13.20
RESIDUAL ACCUMULATION RATE:         2.5749E-05     0.00
----------------------------------------------------------------------
* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.

EXAMS > LIST 17

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: p-CRESOL
ECOSYSTEM: OLIGOTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
----------------------------------------------------------------------
TABLE 17.  EXPOSURE ANALYSIS SUMMARY.
----------------------------------------------------------------------
EXPOSURE:
 A. MAXIMUM CONC. IN WATER COLUMN: 0.36     MG/L DISSOLVED, 0.36     TOT
    MAX. CONC. IN BOTTOM SEDIMENT: 0.11     MG/L DISSOLVED IN PORE WATER
 B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON:  7.2     UG/G
                                       BENTHOS:   2.2     UG/G
 C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS:  1.2     MG/KG (DRY WEIGHT)
FATE:
 A. TOTAL STEADY-STATE ACCUMULATION: 1.88E+03 KG; 98.85% IN WATER COL.,
       1.15% IN BOTTOM SEDIMENTS.
 B. TOTAL LOAD:  13.     KG/DAY - DISPOSITION:  25.22% VIA CHEMICAL
      TRANSFORMATIONS,  12.59% BIOTRANSFORMED,   1.93% VOLATILIZED,
       60.26% EXPORTED VIA OTHER PATHWAYS.
PERSISTENCE:
 A. AT THE END OF A  192.     DAY RECOVERY PERIOD, THE WATER COLUMN HAD
      LOST  72.72% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD
      LOST  63.21% OF THEIR INITIAL BURDEN (  72.62% REMOVAL OVERALL).
 B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY 17. MONTHS.
```

```
EXAMS > PLOT
Enter POINT, PROFIL, HELP or EXIT > HELP
The following options are available:
               POINT   - Vertical profile of the TOS concentration
               PROFILE - Longitudinal profile of the TOS conc.
               HELP    - This message
               EXIT    - Return to the Exams prompt.
Enter POINT, PROFIL, HELP or EXIT > POI
Enter TOTAL, DISSOLVED, PARTICULATES, BIOTA, MASS, HELP or EXIT > HE
The following concentration options are available:
               TOTAL       - mg/l in water column,
                             mg/kg in benthic sediments.
               DISSOLVED   - dissolved mg/l.
               PARTICULATE - sediment-sorbed mg/kg
               BIOTA       - biosorbed ug/g.
               MASS        - toxicant mass as grams/sq. meter AREA.
               HELP        - This message.
               EXIT        - Return to the Exams prompt.
Enter TOTAL, DISSOLVED, PARTICULATES, BIOTA, MASS, HELP or EXIT > DISS
Enter AVE, MAX, MIN, MINMAX, HELP or EXIT > HELP
The following statistical options are available:
               MAX    - For maximum concentration.
               MIN    - For minimum concentration.
               AVE    - For average concentration.
               MINMAX - For simultaneous plot of maxima and minima.
               HELP   - This message.
               EXIT   - Return to the Exams prompt.
Enter AVE, MAX, MIN, MINMAX, HELP or EXIT > MAX

     0.4000     -I
                 I
                 I
                 I 11111111111
  C              I 1         1
  O  0.3200     -I 1         1
  N              I 1    D    1      D
M C              I 1    I    1      I
A E              I 1    S    1      S
X N              I 1    S    1      S
I T  0.2400     -I 1    O    1      O
M R              I 1    L    1      L
A A              I 1    V    1      V
  T              I 1    E    1      E
  I              I 1    D    1      D
  O  0.1600     -I 1         1
  N              I 1    M    1      M
                 I 1    G    1      G
                 I 1    /    1      /
                 I 1    L    1 55555L55555
     0.8000E-01 -+_11111111111_55555555555
                     WAT COL     BOT SED
```

```
EXAMS > PLOT PROF DISS

Enter WATER, SEDIMENTS, HELP or EXIT > HELP
The following options are available:

               WATER     - Water column concentrations.
               SEDIMENTS - Bottom sediment concentrations.
               HELP      - This message.
               EXIT      - Return to the Exams prompt.

Enter WATER, SEDIMENTS, HELP or EXIT > WATER



     0.3650     -I
                 I
                 I LLLLLLLLLLL
                 I 1         1
D C              I 1         1
I O  0.3570     -I 1         1
S N              I 1         1
S C              I 1         1
O E              I 1         1
L N              I 1         1
V T  0.3490     -I 1         1
E R              I 1         1
D A              I 1         1
  T              I 1         1
M I              I 1         1
G O  0.3410     -I 1         1
/ N              I 1         1 EEEEEEEEEEE
L                I 1         1 3         3
                 I 1         1 3         3             LLLLLLLLLLL
                 I 1         1 3         3             6         6
     0.3330     -+_11111111111_33333333333_44444444444_66666666666
                     WATER COLUMN
```

```
EXAMS > ENV IS EUTR

Selected environment is: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST
                         DEFINITION

EXAMS > RUN

No load specified.
Simulation not performed.

EXAMS > CH STRLD(1) TO 0.5
EXAMS > CH NPSLD(6) TO .05
EXAMS > RUN

Simulation beginning for:
Compound: p-CRESOL
Environment: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
with a load of (kg/hr) >  0.5500000
Run complete.

EXAMS > LIST 15

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: p-CRESOL
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
-----------------------------------------------------------------
TABLE 15.  ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.
-----------------------------------------------------------------
            PROCESS              MASS FLUX   % OF LOAD   HALF-LIFE*
                                   KG/HR                   HOURS
      ----------------------     ---------   ---------   ---------
      HYDROLYSIS                 0.0000         0.00        ---
      OXIDATION                  4.7950E-03     0.87       7893.
      PHOTOLYSIS                 1.0320E-04     0.02     3.6671E+05
   ALL CHEMICAL PROCESSES        4.8982E-03     0.89       7726.
-----------------------------------------------------------------
      WATER COLUMN (BACTERIA)    0.5381        97.83       69.79
      BOTTOM SEDIMENTS (BACTERIA) 4.3094E-04    0.08       684.3
   TOTAL BIOLYSIS                0.5385        97.91       70.28
-----------------------------------------------------------------
      VOLATILIZATION             3.6674E-04     0.07     1.0319E+05
      WATER-BORNE EXPORT         6.2519E-03     1.14       6053.
-----------------------------------------------------------------
TRANSFORMATION AND TRANSPORT     0.5500       100.00
TOTAL SYSTEM LOAD                0.5500
RESIDUAL ACCUMULATION RATE:      1.1921E-07     0.00
-----------------------------------------------------------------
* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.

EXAMS > PRINT 15

Requested report has been spooled to printer.
```

```
EXAMS > LIST 17
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: p-CRESOL
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
----------------------------------------------------------------------
TABLE 17.  EXPOSURE ANALYSIS SUMMARY.
----------------------------------------------------------------------
EXPOSURE:
 A. MAXIMUM CONC. IN WATER COLUMN: 2.51E-02 MG/L DISSOLVED, 2.52E-02 TOT
    MAX. CONC. IN BOTTOM SEDIMENT: 2.26E-03 MG/L DISSOLVED IN PORE WATER
 B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON: 0.50      UG/G
                                       BENTHOS:  4.52E-02 UG/G
 C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS: 2.35E-02 MG/KG (DRY WEIGHT)
FATE:
 A. TOTAL STEADY-STATE ACCUMULATION:  55.      KG; 99.22% IN WATER COL.,
       0.78% IN BOTTOM SEDIMENTS.
 B. TOTAL LOAD: 0.55      KG/HOUR - DISPOSITION:   0.89% VIA CHEMICAL
      TRANSFORMATIONS,  97.91% BIOTRANSFORMED,   0.07% VOLATILIZED,
        1.14% EXPORTED VIA OTHER PATHWAYS.
PERSISTENCE:
 A. AT THE END OF A  132.      HOUR RECOVERY PERIOD, THE WATER COLUMN HAD
      LOST  46.42% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD
      LOST   5.74% OF THEIR INITIAL BURDEN (  46.11% REMOVAL OVERALL).
 B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY 33. DAYS.

EXAMS > PRINT 17
Requested report has been spooled to printer.

EXAMS > PLOT PROF DIS WAT

     0.2600E-01 -I
                 I LLLLLLLLLLL
                 I 1         1
                 I 1         1
D C              I 1         1
I O  0.2100E-01 -I 1         1
S N              I 1         1
S C              I 1         1
O E              I 1         1
L N              I 1         1
V T  0.1600E-01 -I 1         1
E R              I 1         1
D A              I 1         1
  T              I 1         1
M I              I 1         1
G O  0.1100E-01 -I 1         1
/ N              I 1         1
L                I 1         1 EEEEEEEEEEE
                 I 1         1 3         3 HHHHHHHHHHH
                 I 1         1 3         3 4         4
     0.6000E-02 -+_11111111111_33333333333_44444444444_66666666666
                     WATER COLUMN
```

```
EXAMS > LIST 13


  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: p-CRESOL
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
-------------------------------------------------------------------------
TABLE 13. DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
-------------------------------------------------------------------------
COMP STEADY-STATE RESIDENT MASS     **** TOXICANT CONCENTRATIONS ****
         2                          TOTAL   DISSOLVED SEDIMENTS   BIOTA
     G/M       KILOS         %       MG/*     MG/L      MG/KG      UG/G
--- ------   ------       ------  --------- --------- --------- ---------
  1 0.126      6.291       11.61  2.517E-02 2.514E-02 0.258     0.501
  3 9.559E-02  23.90       44.11  9.559E-03 9.558E-03 9.798E-02 0.191
  4 8.956E-02  22.39       41.33  8.956E-03 8.955E-03 9.012E-02 0.179
  6 3.190E-02  1.595        2.94  6.380E-03 6.374E-03 6.533E-02 0.127
 SUBTOTAL:     54.17       99.22
 AND IN THE BOTTOM SEDIMENTS:
  2 4.660E-04 2.3298E-02    5.48  6.901E-03 6.603E-04 6.608E-03 1.320E-02
  5 1.585E-03 0.3963       93.14  2.348E-02 2.261E-03 2.263E-02 4.522E-02
  7 1.181E-04 5.9065E-03    1.39  1.750E-03 1.674E-04 1.675E-03 3.348E-03
 SUBTOTAL:    0.4255        0.78
TOTAL MASS (KILOGRAMS) =      54.60
-------------------------------------------------------------------------
* TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.

EXAMS > QUIT
JOB11 -- STOP

17:44:02  SIZE: 31K  CPU: 50.63  STATUS: SUCCESS

PDS > LOGOUT
```

3.3.2 Tutorial Session #2: Entering New Data; Analyzing Persistence

Objectives: Use of CHANGE, COMPOUND, and STORE commands to enter chemical data, investigating properties of chemicals with EXAMS.

The compound is "XXX", a chemical that has recently been synthesized but has seen no use in commerce. Its molecular weight is 263.4, it is soluble in water to 0.15 ppm, has a vapor pressure of 0.02 Torr, and has an apparent partition coefficient on sediments of about 1000. The results of partitioning experiments, however, were not entirely satisfactory; in fact the partition coefficient may be as low as 100 or as high as 10,000.

The objective of this EXAMS run is to determine, for this "persistent" (by definition, at least for the moment, as no indication of degradability is available), the actual degree to which the material would persist in lake ecosystems, and the magnitude of volatilization losses to be expected given a unit loading. Furthermore, the uncertainty in the partition coefficient is of unknown significance to the conclusions, so EXAMS interactive capabilities will be called upon to perform a sensitivity analysis of this question.

```
PDS> RUN EXAMS
22:36:12
          Welcome to EXAMS
   EXposure Analysis Modeling System
Athens Environmental Research Laboratory
    Released for field trials Jan-81

The ATHENS collection of compounds is available for your use.

EXAMS > SHOW COMPOUNDS

    CHEMICAL NAME                        COMMON NAME

  1 UNSPECIFIED CHEMICAL                  UNS
  2 9H-CARBAZOLE                          CAR
  3 BENZO[f]QUINOLINE                     BFQ
  4 7H-DIBENZO[c,g]CARBAZOLE              DBC
  5 BENZO[b]THIOPHENE                     BT
  6 DIBENZOTHIOPHENE                      DBT
  7 BENZ[a]ANTHRACENE                     BA
  8 p-CRESOL                              PCR
  9 BENZO[a]PYRENE                        BAP
 10 MIREX                                 MIR
 11 METHYL PARATHION                      MP
 12 QUINOLINE                             QUI
```

```
EXAMS > COMP IS UNS
Compound selected > Unspecified Chemical

EXAMS > HELP VARIABLES
The chemical and environmental data used for EXAMS' computations are
continually available for inspection and alteration by the interactive
user.  The data can be inspected in tabular form (type <HELP SHOW> for a
description), or the current value of any single datum can be SHOWn.
For example,    EXAMS > SHOW PH(4)  will return:  PH IS  7.000  when
the pH of compartment number 4 is 7.0.  A description of each block of
data (ADVECTION/CHEMISTRY/GEOMETRY/GLOBALS/LOADS/QUALITY/TURBULENCE) is
given under <HELP <KEYWORD>> where <KEYWORD> is the name of one of these
blocks.  Typing <HELP <nnn>> where <nnn> is the name of an input datum
will elicit a definition of the variable (e.g. <HELP PH>); also see
<DESCRIBE>.  When CHANGEing or SHOWing a variable, the vector/matrix
indices must be entered in the proper (row,column) order (because
<nnn(1,3)> is by no means equivalent to <nnn(3,1)>).  In a system
that can handle 10-compartment ecosystems, the dimensions of variables
include the values: (5), (3,5), (10), (30), (5,39), and (39).  Dimension
(5) refers to the chemical species of the toxicant (c.f. <HELP SPFL>);
dimension (3) refers to physical forms (1: dissolved, 2: sediment-
sorbed, 3: biosorbed); dimension (3,5) to matrices of molecular
configurations amalgamating (3) and (5) (e.g. <nnn(3,1)> refers to a
biosorbed neutral molecule); dimension (10) to ecosystem compartments;
dimension (30) to compartment interconnections; and dimension (39)
refers to irradiance and light absorption intervals (see Table 2.18).

EXAMS > HELP SOL
SOL is a REAL VECTOR with 5 rows.
Aqueous solubility of toxicant chemical species.  If the corresponding
value in vector ESOL (c.f.) is zero, SOL(K) is interpreted as an
aqueous solubility in mg/liter.  If ESOL(K) is non-zero, SOL(K) is
interpreted as the base-10 logarithm of the pre-exponential factor in
an equation (Eq. 2.95) describing the molar solubility of the toxicant
species as a function of environmental temperature (TCEL).  The vector
indices for SOL are given in the text describing ESOL.  Solubilities
are used (inter alia) to limit the permissible external loadings of
the toxicant on the system to values consonant with model assuptions.
Units: mg/liter

EXAMS > HELP ESOL
ESOL is a REAL VECTOR with 5 rows.
Enthalpy term for describing solubility of the
toxicant as a function of temperature.
ESOL(1) - datum for solubility of SH2
ESOL(2) - datum for solubility of SH3+
ESOL(3) -   "     "      "      "  SH4++
ESOL(4) -   "     "      "      "  SH-
ESOL(5) -   "     "      "      "  S=
Units: kcal/mole

EXAMS > CHANGE SOL(1) TO 0.15
EXAMS > CH MWT TO 263.4

EXAMS > SHO MWT

MWT IS   263.4

EXAMS > DESCRIBE VAPR
VAPR is a REAL SCALAR.

EXAMS > CH VAPR TO 2.E-2

EXAMS > HELP KPS
KPS is a REAL VECTOR with 5 rows.
Partition coefficients for computing sorption of toxicant on
compartment sediments.  The chemical species signified by each
of the values entered in the vector is defined in the text for
parameter ESOL.
Units: (mg/kg)/(mg/liter)

EXAMS > CHAN KPS(1) TO 100.

EXAMS > COMPOUND NAME IS XXX WITH KPS=100.

EXAMS > SHOW CHEMISTRY
Compound characteristics for > XXX WITH KPS=100.

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: XXX WITH KPS=100.
ECOSYSTEM: Unspecified Environment
-----------------------------------------------------------------------
TABLE 1.1.  SH2 (NEUTRAL MOLECULE, SPECIES  1) INPUT DATA.
MWT=  263.4      SOL = 0.1500      VAPR= 2.0000E-02 HENRY= 0.0000
KVO= 0.0000      ESOL= 0.0000      EVPR= 0.0000     EHEN = 0.0000
KPS=  100.0      KPB = 0.0000      KOC = 0.0000     KOW  = 0.0000
KAH1= 0.0000      EAH1= 0.0000      KNH1= 0.0000      ENH1= 0.0000
KAH2= 0.0000      EAH2= 0.0000      KNH2= 0.0000      ENH2= 0.0000
KAH3= 0.0000      EAH3= 0.0000      KNH3= 0.0000      ENH3= 0.0000
KBH1= 0.0000      EBH1= 0.0000      KOX1= 0.0000      EOX1= 0.0000
KBH2= 0.0000      EBH2= 0.0000      KOX2= 0.0000      EOX2= 0.0000
KBH3= 0.0000      EBH3= 0.0000      KOX3= 0.0000      EOX3= 0.0000
KBACW1= 0.0000      QTW1= 0.0000      KBACS1= 0.0000      QTS1= 0.0000
KBACW2= 0.0000      QTW2= 0.0000      KBACS2= 0.0000      QTS2= 0.0000
KBACW3= 0.0000      QTW3= 0.0000      KBACS3= 0.0000      QTS3= 0.0000
KDP= 0.0000      RFLAT= 0.0000      LAMAX=     0.00
QUANT1= 0.0000      QUANT2= 0.0000      QUANT3= 0.0000
ABSORPTION SPECTRUM (ABS):   0.0000         0.0000         0.0000
 0.0000         0.0000         0.0000         0.0000         0.0000         0.0000
 0.0000         0.0000         0.0000         0.0000         0.0000         0.0000
 0.0000         0.0000         0.0000         0.0000         0.0000         0.0000
 0.0000         0.0000         0.0000         0.0000         0.0000         0.0000
 0.0000         0.0000         0.0000         0.0000         0.0000         0.0000
 0.0000         0.0000         0.0000         0.0000         0.0000         0.0000
```

```
EXAMS > ENVIR IS EUTR

Selected environment is: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST
DEFINITION


EXAMS > CH STRLD(1) TO 1.0

EXAMS > RUN

Simulation beginning for:
Compound: XXX WITH KPS=100.
Environment: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
with a load of (kg/hr) >   1.000000
STREAM LOADING EXCEEDED SOLUBILITY LIMIT IN ELEMENT  1.
LOAD HAS BEEN ADJUSTED.

Run complete.

EXAMS > SHO LOADS

Environment: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
Compartments (KOUNT):  7
                                 1  2  3  4  5  6  7
Type of compartment (TYPEE):  L  B  E  H  B  L  B

TABLE 12.  TOXICANT LOADINGS (KG/HR) BY SYSTEM ELEMENT.
--------------------------------------------------------------------------
ELEMENT  STREAM FLOW    RAINFALL    INTERFLOW    NPS LOAD    DRIFT LOAD
-------  -----------  ----------  ----------  ----------  ----------
   1      1.8337E-02
   2
   3
   4
   5
   6
   7
--------------------------------------------------------------------------


EXAMS > SHOW USER COMP

No user defined compounds in the library.

EXAMS > STORE COMP 7

Compound stored > XXX WITH KPS=100.
```

```
EXAMS > LIST 17
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: XXX WITH KPS=100.
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
-------------------------------------------------------------------------
TABLE 17.  EXPOSURE ANALYSIS SUMMARY.
-------------------------------------------------------------------------
EXPOSURE:
 A. MAXIMUM CONC. IN WATER COLUMN: 2.91E-03 MG/L DISSOLVED, 2.91E-03 TOT
    MAX. CONC. IN BOTTOM SEDIMENT: 1.43E-03 MG/L DISSOLVED IN PORE WATER
 B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON: 0.00      UG/G
                                        BENTHOS:  0.00      UG/G
 C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS: 0.14      MG/KG (DRY WEIGHT)
FATE:
 A. TOTAL STEADY-STATE ACCUMULATION:  11.      KG; 75.36% IN WATER COL.,
       24.64% IN BOTTOM SEDIMENTS.
 B. TOTAL LOAD: 0.44      KG/DAY - DISPOSITION:   0.00% VIA CHEMICAL
      TRANSFORMATIONS,   0.00% BIOTRANSFORMED,  92.57% VOLATILIZED,
        7.43% EXPORTED VIA OTHER PATHWAYS.
PERSISTENCE:
 A. AT THE END OF A  36.0      DAY RECOVERY PERIOD, THE WATER COLUMN HAD
      LOST  73.23% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD
      LOST  17.29% OF THEIR INITIAL BURDEN (  59.45% REMOVAL OVERALL).
 B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY  8. MONTHS.

EXAMS > LIST 15
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: XXX WITH KPS=100.
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
-------------------------------------------------------------------------
TABLE 15.  ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.
-------------------------------------------------------------------------
             PROCESS                  MASS FLUX     % OF LOAD    HALF-LIFE*
                                       KG/DAY                      DAYS
      -----------------------         ---------     ---------    ---------
      HYDROLYSIS                      0.0000          0.00          ---
      OXIDATION                       0.0000          0.00          ---
      PHOTOLYSIS                      0.0000          0.00          ---
  ALL CHEMICAL PROCESSES              0.0000          0.00          ---
-------------------------------------------------------------------------
      WATER COLUMN (BACTERIA)         0.0000          0.00          ---
      BOTTOM SEDIMENTS (BACTERIA)     0.0000          0.00          ---
  TOTAL BIOLYSIS                      0.0000          0.00          ---
-------------------------------------------------------------------------
      VOLATILIZATION                  0.4074         92.57         19.51
      WATER-BORNE EXPORT              3.2680E-02      7.43         243.3
-------------------------------------------------------------------------
TRANSFORMATION AND TRANSPORT          0.4401        100.00
TOTAL SYSTEM LOAD                     0.4401
RESIDUAL ACCUMULATION RATE:           4.4703E-08      0.00
-------------------------------------------------------------------------
* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.
```

```
EXAMS > CH KPS(1) TO 1000.

EXAMS > COMP NAME IS XXX WITH KPS=1000.

EXAMS > RUN

Simulation beginning for:
Compound: XXX WITH KPS=1000.
Environment: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
with a load of (kg/hr) >  0.1833750E-01

Run complete.

EXAMS > LIST 17
```

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: XXX WITH KPS=1000.
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
-----------------------------------------------------------------------
TABLE 17.  EXPOSURE ANALYSIS SUMMARY.
-----------------------------------------------------------------------
EXPOSURE:
 A. MAXIMUM CONC. IN WATER COLUMN: 2.91E-03 MG/L DISSOLVED, 2.92E-03 TOT
    MAX. CONC. IN BOTTOM SEDIMENT: 2.64E-03 MG/L DISSOLVED IN PORE WATER
 B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON: 0.00     UG/G
                                        BENTHOS:  0.00     UG/G
 C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS:  2.6     MG/KG (DRY WEIGHT)
FATE:
 A. TOTAL STEADY-STATE ACCUMULATION:  47.     KG; 18.52% IN WATER COL.,
       81.48% IN BOTTOM SEDIMENTS.
 B. TOTAL LOAD: 0.44      KG/DAY - DISPOSITION:   0.00% VIA CHEMICAL
      TRANSFORMATIONS,   0.00% BIOTRANSFORMED,  92.57% VOLATILIZED,
        7.43% EXPORTED VIA OTHER PATHWAYS.
PERSISTENCE:
 A. AT THE END OF A  144.     DAY RECOVERY PERIOD, THE WATER COLUMN HAD
      LOST  69.81% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD
      LOST  42.38% OF THEIR INITIAL BURDEN (  47.46% REMOVAL OVERALL).
 B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY 27. MONTHS.

EXAMS > LIST 15

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: XXX WITH KPS=1000.
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
-----------------------------------------------------------------------
TABLE 15.  ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.
-----------------------------------------------------------------------
             PROCESS                 MASS FLUX   % OF LOAD   HALF-LIFE*
                                      KG/DAY                   DAYS
     ----------------------         ---------   ---------   ---------
     HYDROLYSIS                     0.0000        0.00         ---
     OXIDATION                      0.0000        0.00         ---
     PHOTOLYSIS                     0.0000        0.00         ---
 ALL CHEMICAL PROCESSES             0.0000        0.00         ---
-----------------------------------------------------------------------
     WATER COLUMN (BACTERIA)        0.0000        0.00         ---
     BOTTOM SEDIMENTS (BACTERIA)    0.0000        0.00         ---
 TOTAL BIOLYSIS                     0.0000        0.00         ---
-----------------------------------------------------------------------
     VOLATILIZATION                 0.4074       92.57        79.43
     WATER-BORNE EXPORT             3.2696E-02    7.43        989.7
-----------------------------------------------------------------------
TRANSFORMATION AND TRANSPORT        0.4401      100.00
TOTAL SYSTEM LOAD                   0.4401
RESIDUAL ACCUMULATION RATE:         4.4703E-08    0.00
-----------------------------------------------------------------------
* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.
```

```
EXAMS > STORE COMPOUND 8

Compound stored > XXX WITH KPS=1000.

EXAMS > CH KPS(1) TO 10000.

EXAMS > COMP NAME IS XXX WITH KPS=10000.

EXAMS > RUN

Simulation beginning for:
Compound: XXX WITH KPS=10000.
Environment: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
with a load of (kg/hr) >  0.1833750E-01

PLEASE BE PATIENT; THE KINETIC EQUATIONS ARE STIFF.

Run complete.

EXAMS > LIST 17

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: XXX WITH KPS=10000.
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
-------------------------------------------------------------------------
TABLE 17.  EXPOSURE ANALYSIS SUMMARY.
-------------------------------------------------------------------------
EXPOSURE:
 A. MAXIMUM CONC. IN WATER COLUMN: 2.91E-03 MG/L DISSOLVED, 2.92E-03 TOT
    MAX. CONC. IN BOTTOM SEDIMENT: 2.88E-03 MG/L DISSOLVED IN PORE WATER
 B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON: 0.00     UG/G
                                        BENTHOS:  0.00     UG/G
 C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS:  29.     MG/KG (DRY WEIGHT)
FATE:
 A. TOTAL STEADY-STATE ACCUMULATION: 4.06E+02 KG;  2.14% IN WATER COL.,
       97.86% IN BOTTOM SEDIMENTS.
 B. TOTAL LOAD:  13.     KG/MONTH - DISPOSITION:   0.00% VIA CHEMICAL
      TRANSFORMATIONS,   0.00% BIOTRANSFORMED,  92.54% VOLATILIZED,
        7.46% EXPORTED VIA OTHER PATHWAYS.
PERSISTENCE:
 A. AT THE END OF A  36.0    MONTH RECOVERY PERIOD, THE WATER COLUMN HAD
      LOST  61.54% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD
      LOST  55.13% OF THEIR INITIAL BURDEN (  55.26% REMOVAL OVERALL).
 B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY    13. YEARS.

EXAMS > STORE COMPOUND 9

Compound stored > XXX WITH KPS=10000.
```

```
EXAMS > LIST 15

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: XXX WITH KPS=10000.
ECOSYSTEM: EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
------------------------------------------------------------------
TABLE 15.  ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.
------------------------------------------------------------------
            PROCESS                MASS FLUX   % OF LOAD   HALF-LIFE*
                                    KG/MONTH                 MONTHS
     -----------------------       ---------   ---------   ---------
     HYDROLYSIS                    0.0000         0.00        ---
     OXIDATION                     0.0000         0.00        ---
     PHOTOLYSIS                    0.0000         0.00        ---
  ALL CHEMICAL PROCESSES           0.0000         0.00        ---
------------------------------------------------------------------
     WATER COLUMN (BACTERIA)       0.0000         0.00        ---
     BOTTOM SEDIMENTS (BACTERIA)   0.0000         0.00        ---
  TOTAL BIOLYSIS                   0.0000         0.00        ---
------------------------------------------------------------------
     VOLATILIZATION                 12.40        92.54       22.68
     WATER-BORNE EXPORT            0.9999         7.46       281.1
------------------------------------------------------------------
TRANSFORMATION AND TRANSPORT        13.40       100.00
TOTAL SYSTEM LOAD                   13.40
RESIDUAL ACCUMULATION RATE:        2.7213E-06     0.00
------------------------------------------------------------------
* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.

EXAMS > STOP
JOB32 -- STOP

22:44:48   Size: 31K  CPU: 58.40  Status: SUCCESS
```

In summary:

KPS	VOLATILIZED FLUX	REMOVAL TIME
100.	0.41 kg/day	0.7 year
1000.	0.41 kg/day	2.2 years
10000.	0.41 kg/day	13. years

The available data for "XXX" have been stored under 3 descriptive names in EXAMS' User Data Base. Upon re-entering the system, these data can be retrieved via the RECALL command, for example:

```
EXAMS > RECALL COMP 8
```

3.3.3. Tutorial Session #3: Sensitivity Analysis

Objectives: using EXAMS for evaluation of rate constant data, and altering ecosystem properties via the CHANGE command. The EXAMS run is designed to elicit the primary degradation pathway of methyl parathion in a 1-hectare pond, investigate the effects of pH (i.e. alkaline hydrolysis) and biolysis rate constants on pollutant kinetics, and run a comparative baseline of methyl parathion behaviour in an oligotrophic lake.

```
PDS> RUN EXAMS
23:50:51
          Welcome to EXAMS
   Exposure Analysis Modeling System
Athens Environmental Research Laboratory
    Released for field trials Jan-81


The ATHENS collection of compounds is available for your use.


EXAMS > COMP IS MP

Compound selected > METHYL PARATHION

EXAMS > ENV IS POND

Selected environment is: POND, AERL DEVELOPMENT PHASE TEST DEFINITION

EXAMS > CHANGE STRLD(1) TO 0.02

EXAMS > COMP NAME IS Methyl Parathion - Baseline

EXAMS > RUN

Simulation beginning for:
Compound: Methyl Parathion - Baseline
Environment: POND, AERL DEVELOPMENT PHASE TEST DEFINITION
with a load of (kg/hr) >  0.2000000E-01

Run complete.

EXAMS > LIST 15

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Methyl Parathion - Baseline
ECOSYSTEM: POND, AERL DEVELOPMENT PHASE TEST DEFINITION
```

```
-----------------------------------------------------------------------
TABLE 15.  ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.
-----------------------------------------------------------------------
             PROCESS                   MASS FLUX    % OF LOAD    HALF-LIFE*
                                        KG/DAY                      DAYS
      -----------------------          ---------    ---------    ---------
      HYDROLYSIS                       7.3110E-03      1.52        666.7
      OXIDATION                        0.0000          0.00        ---
      PHOTOLYSIS                       4.6392E-03      0.97        1051.
  ALL CHEMICAL PROCESSES               1.1950E-02      2.49        407.9
-----------------------------------------------------------------------
      WATER COLUMN (BACTERIA)          0.3498         72.87        6.318
      BOTTOM SEDIMENTS (BACTERIA)      1.6757E-02      3.49        159.0
  TOTAL BIOLYSIS                       0.3665         76.36        13.30
-----------------------------------------------------------------------
      VOLATILIZATION                   9.1247E-05      0.02      5.3415E+04
      WATER-BORNE EXPORT               0.1014         21.13        48.05
-----------------------------------------------------------------------
TRANSFORMATION AND TRANSPORT           0.4800        100.00
TOTAL SYSTEM LOAD                      0.4800
RESIDUAL ACCUMULATION RATE:            4.4703E-08      0.00
-----------------------------------------------------------------------
* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.

EXAMS > SHOW CHEM
Compound characteristics for > Methyl Parathion - Baseline
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Methyl Parathion - Baseline
ECOSYSTEM: POND, AERL DEVELOPMENT PHASE TEST DEFINITION
-----------------------------------------------------------------------
TABLE 1.1.  SH2 (NEUTRAL MOLECULE, SPECIES  1) INPUT DATA.
MWT=  263.1       SOL =  50.00       VAPR=  14.37       HENRY= 0.0000
KVO= 0.0000       ESOL= 0.0000       EVPR=  26.11       EHEN = 0.0000
KPS=  50.00       KPB =  371.5       KOC = 0.0000       KOW  = 0.0000
KAH1= 0.0000       EAH1= 0.0000        KNH1=  13.66       ENH1=  23.40
KAH2= 0.0000       EAH2= 0.0000        KNH2= 0.0000       ENH2= 0.0000
KAH3= 0.0000       EAH3= 0.0000        KNH3= 0.0000       ENH3= 0.0000
KBH1=  17.69       EBH1=  22.00        KOX1= 0.0000       EOX1= 0.0000
KBH2= 0.0000       EBH2= 0.0000        KOX2= 0.0000       EOX2= 0.0000
KBH3= 0.0000       EBH3= 0.0000        KOX3= 0.0000       EOX3= 0.0000
KBACW1= 4.6000E-08 QTW1= 0.0000       KBACS1= 4.6000E-08 QTS1= 0.0000
KBACW2= 0.0000     QTW2= 0.0000       KBACS2= 0.0000     QTS2= 0.0000
KBACW3= 0.0000     QTW3= 0.0000       KBACS3= 0.0000     QTS3= 0.0000
KDP= 0.0000      RFLAT=  40.00      LAMAX=      0.00
QUANT1= 1.7000E-04 QUANT2= 0.0000     QUANT3= 0.0000
ABSPRPTION SPECTRUM (ABS):      6040.        5460.        4930.
 4310.        3700.        3210.        2760.        2290.        1920.
 1630.        1310.        933.0        568.0        374.0        244.0
 145.0        82.00        45.00        9.000        0.0000       0.0000
0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
```

```
EXAMS > SHOW

Enter one of the following options:
      COMPOUNDS,
      CHEMISTRY,
      ENVIRONMENT,
      GEOMETRY,
      ADVECTION,
      TURBULANCE,
      QUALITY,
      GLOBALS,
      LOADS,
      USER,
      HELP or
      EXIT > QUALITY

Environment: POND, AERL DEVELOPMENT PHASE TEST DEFINITION
Compartments (KOUNT):  2
                                 1  2
Type of compartment (TYPEE):  L  B

Compartment No.  1

FROC  =  0.1000     CEC    =   25.00
AEC   =   25.00     TCEL   =   15.00
PH    =   8.000     POH    =   6.000
OXRAD =  1.0000E-09 BIOMS  =   12.90
PLRA  =  3.1000E-02 BIOTM  =   15.00
BACTO =  1.0000E+05 ACBAC  =   1.000
KO2   =   8.000     CMPET  =   2.000
DOC   =  0.5000     DFAC   =   1.190
CHL   =  2.0000E-03

Would you like information for compartment No.  2
Enter (Y, N or Q to quit) > Y

Environment: POND, AERL DEVELOPMENT PHASE TEST DEFINITION
Compartments (KOUNT):  2
                                 1  2
Type of compartment (TYPEE):  L  B

Compartment No.  2

FROC  =  0.1000     CEC    =   25.00
AEC   =   25.00     TCEL   =   15.00
PH    =   6.000     POH    =   8.000
OXRAD =  0.0000     BIOMS  =   50.01
PLRA  =  1.2000E-04 BIOTM  =   15.00
BACTO =  2.0000E+07 ACBAC  =   1.000

EXAMS > CHANGE PH(*) TO 10.
EXAMS > HELP POH
POH is a REAL VECTOR with 10 rows.
The negative value of the power to which 10 is raised in order to
obtain the temporally averaged concentration of hydroxide [OH-] ions
in gram-molecules per liter.
Units: pOH units

EXAMS > CH POH(*) TO 4

EXAMS > ENVIR NAME IS Alkaline Pond - enhanced hydrolysis

EXAMS > STORE ENVIRON 5

Environment stored: Alkaline Pond - enhanced hydrolysis

EXAMS > RUN

Simulation beginning for:
Compound: Methyl Parathion - Baseline
Environment: Alkaline Pond - enhanced hydrolysis
with a load of (kg/hr) >  0.2000000E-01

Run complete.

EXAMS > LIST 15

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Methyl Parathion - Baseline
ECOSYSTEM: Alkaline Pond - enhanced hydrolysis
-----------------------------------------------------------------------
TABLE 15.  ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.
-----------------------------------------------------------------------
             PROCESS                MASS FLUX    % OF LOAD   HALF-LIFE*
                                     KG/DAY                     DAYS
      ------------------------      ---------    ---------   ---------
      HYDROLYSIS                    7.4498E-02     15.52      55.85
      OXIDATION                     0.0000          0.00        ---
      PHOTOLYSIS                    3.9811E-03      0.83      1045.
  ALL CHEMICAL PROCESSES            7.8479E-02     16.35      53.01
-----------------------------------------------------------------------
      WATER COLUMN (BACTERIA)       0.3002         62.53      6.318
      BOTTOM SEDIMENTS (BACTERIA)   1.4240E-02      2.97      159.0
  TOTAL BIOLYSIS                    0.3144         65.50      13.23
-----------------------------------------------------------------------
      VOLATILIZATION                7.8304E-05      0.02     5.3131E+04
      WATER-BORNE EXPORT            8.7048E-02     18.13      47.79
-----------------------------------------------------------------------
TRANSFORMATION AND TRANSPORT        0.4800        100.00
TOTAL SYSTEM LOAD                   0.4800
RESIDUAL ACCUMULATION RATE:         4.4703E-08      0.00
-----------------------------------------------------------------------
* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.
```

```
EXAMS > ENV IS POND

Selected environment is: POND, AERL DEVELOPMENT PHASE TEST DEFINITION

EXAMS > CHANGE SRTLD(1) TO 0.02

Unrecognized variable name.

EXAMS > CH STRLD(1) TO 0.02

EXAMS > RUN

Simulation beginning for:
Compound: Methyl Parathion - Baseline
Environment: POND, AERL DEVELOPMENT PHASE TEST DEFINITION
with a load of (kg/hr) >  0.2000000E-01

Run complete.

EXAMS > LIST 17

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Methyl Parathion - Baseline
ECOSYSTEM: POND, AERL DEVELOPMENT PHASE TEST DEFINITION
-----------------------------------------------------------------------
TABLE 17.  EXPOSURE ANALYSIS SUMMARY.
-----------------------------------------------------------------------
EXPOSURE:
 A. MAXIMUM CONC. IN WATER COLUMN: 0.16     MG/L DISSOLVED, 0.16     TOT
    MAX. CONC. IN BOTTOM SEDIMENT: 0.11     MG/L DISSOLVED IN PORE WATER
 B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON:  59.      UG/G
                                       BENTHOS:   42.      UG/G
 C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS:  5.7      MG/KG (DRY WEIGHT)
FATE:
 A. TOTAL STEADY-STATE ACCUMULATION:  7.0      KG; 45.34% IN WATER COL.,
       54.66% IN BOTTOM SEDIMENTS.
 B. TOTAL LOAD: 0.48     KG/DAY - DISPOSITION:   2.49% VIA CHEMICAL
      TRANSFORMATIONS,  76.36% BIOTRANSFORMED,   0.02% VOLATILIZED,
       21.13% EXPORTED VIA OTHER PATHWAYS.
PERSISTENCE:
 A. AT THE END OF A  24.0      DAY RECOVERY PERIOD, THE WATER COLUMN HAD
      LOST  90.03% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD
      LOST  25.72% OF THEIR INITIAL BURDEN (  54.87% REMOVAL OVERALL).
 B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY  6. MONTHS.

EXAMS > CHA KBACW(1,1) TO 4.6E-7

EXAMS > COMP NAME IS Methyl Parathion with HIGH biolysis.
EXAMS > STORE COMP 3

Compound stored > Methyl Parathion with HIGH biolysis.

EXAMS > RUN

Simulation beginning for:
Compound: Methyl Parathion with HIGH biolysis.
Environment: POND, AERL DEVELOPMENT PHASE TEST DEFINITION
with a load of (kg/hr) >  0.2000000E-01

Run complete.

EXAMS > LIST 17

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Methyl Parathion with HIGH biolysis.
ECOSYSTEM: POND, AERL DEVELOPMENT PHASE TEST DEFINITION
------------------------------------------------------------------------
TABLE 17.  EXPOSURE ANALYSIS SUMMARY.
------------------------------------------------------------------------
EXPOSURE:
 A. MAXIMUM CONC. IN WATER COLUMN: 2.10E-02 MG/L DISSOLVED, 2.11E-02 TOT
    MAX. CONC. IN BOTTOM SEDIMENT: 1.49E-02 MG/L DISSOLVED IN PORE WATER
 B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON:  7.8      UG/G
                                       BENTHOS:   5.5      UG/G
 C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS: 0.75      MG/KG (DRY WEIGHT)
FATE:
 A. TOTAL STEADY-STATE ACCUMULATION: 0.93      KG; 45.34% IN WATER COL.,
       54.66% IN BOTTOM SEDIMENTS.
 B. TOTAL LOAD: 2.00E-02 KG/HOUR - DISPOSITION:   0.33% VIA CHEMICAL
      TRANSFORMATIONS,  96.87% BIOTRANSFORMED,   0.00% VOLATILIZED,
        2.80% EXPORTED VIA OTHER PATHWAYS.
PERSISTENCE:
 A. AT THE END OF A  60.0     HOUR RECOVERY PERIOD, THE WATER COLUMN HAD
      LOST  93.05% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD
      LOST   3.04% OF THEIR INITIAL BURDEN (  43.85% REMOVAL OVERALL).
 B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY  5. MONTHS.


EXAMS > CH KBACW(1,1) TO 4.6E-9

EXAMS > COMP NAME IS Methyl Parathion with LOW biolysis.

EXAMS > STORE COMP 4

Compound stored > Methyl Parathion with LOW biolysis.
```

```
EXAMS > RUN

Simulation beginning for:
Compound: Methyl Parathion with LOW biolysis.
Environment: POND, AERL DEVELOPMENT PHASE TEST DEFINITION
with a load of (kg/hr) >  0.2000000E-01

Run complete.

EXAMS > LIST 17

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Methyl Parathion with LOW biolysis.
ECOSYSTEM: POND, AERL DEVELOPMENT PHASE TEST DEFINITION
---------------------------------------------------------------------------
TABLE 17.  EXPOSURE ANALYSIS SUMMARY.
---------------------------------------------------------------------------
EXPOSURE:
 A. MAXIMUM CONC. IN WATER COLUMN: 0.46      MG/L DISSOLVED, 0.46      TOT
    MAX. CONC. IN BOTTOM SEDIMENT: 0.33      MG/L DISSOLVED IN PORE WATER
 B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON: 1.71E+02 UG/G
                                        BENTHOS:  1.21E+02 UG/G
 C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS:  17.      MG/KG (DRY WEIGHT)
FATE:
 A. TOTAL STEADY-STATE ACCUMULATION:  20.      KG; 45.34% IN WATER COL.,
       54.66% IN BOTTOM SEDIMENTS.
 B. TOTAL LOAD: 0.48      KG/DAY - DISPOSITION:   7.23% VIA CHEMICAL
      TRANSFORMATIONS,  31.31% BIOTRANSFORMED,   0.06% VOLATILIZED,
       61.40% EXPORTED VIA OTHER PATHWAYS.
PERSISTENCE:
 A. AT THE END OF A  60.0     DAY RECOVERY PERIOD, THE WATER COLUMN HAD
      LOST  82.20% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD
      LOST  44.62% OF THEIR INITIAL BURDEN (  61.66% REMOVAL OVERALL).
 B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY  8. MONTHS.
```

Summary (not a machine output) -- Pond biolysis analysis

Rate Constant	Exposure Concentration (mg/L)
LOW	0.46
BASELINE	0.16
HIGH	0.021

```
Restart computations for oligotrophic lake comparison:

EXAMS > COMP IS MP

Compound selected > METHYL PARATHION

EXAMS > COMPOUND NAME IS Methyl Parathion - Baseline.

EXAMS > ENV IS OLIG
Selected environment is: OLIGOTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST
DEFINITION

EXAMS > CHA STRLD(1) TO 1.0

EXAMS > RUN

Simulation beginning for:
Compound: Methyl Parathion - Baseline.
Environment: OLIGOTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
with a load of (kg/hr) >   1.000000

Run complete.

EXAMS > LIST 15

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Methyl Parathion - Baseline.
ECOSYSTEM: OLIGOTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
------------------------------------------------------------------------
TABLE 15.  ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.
------------------------------------------------------------------------
           PROCESS                 MASS FLUX    % OF LOAD    HALF-LIFE*
                                    KG/DAY                      DAYS
      ----------------------     ---------    ---------    ---------
      HYDROLYSIS                   1.861          7.75       572.5
      OXIDATION                  0.0000          0.00        ---
      PHOTOLYSIS                   16.26         67.77       65.49
  ALL CHEMICAL PROCESSES           18.12         75.52       58.77
------------------------------------------------------------------------
      WATER COLUMN (BACTERIA)    0.1717          0.72       5499.
      BOTTOM SEDIMENTS (BACTERIA) 8.4649E-04     0.00       1.4300E+05
  TOTAL BIOLYSIS                 0.1725          0.72       6174.
------------------------------------------------------------------------
      VOLATILIZATION             1.4732E-02     0.06       7.2304E+04
      WATER-BORNE EXPORT           5.688         23.70       187.3
------------------------------------------------------------------------
TRANSFORMATION AND TRANSPORT       24.00        100.00
TOTAL SYSTEM LOAD                  24.00
RESIDUAL ACCUMULATION RATE:      8.5831E-06     0.00
------------------------------------------------------------------------
* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.
```

```
EXAMS > LIST 10

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Methyl Parathion - Baseline.
ECOSYSTEM: OLIGOTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
-------------------------------------------------------------------------
TABLE 10.  KINETIC PROFILE OF ORGANIC TOXICANT.  RATE CONSTANTS DERIVED
FROM COUPLING OF TOXICANT CHARACTERISTICS TO ECOSYSTEM PROPERTIES.
-------------------------------------------------------------------------
CP T*  ----------- PSEUDO-FIRST-ORDER RATE CONSTANTS (/HR) -----------
   Y   HYDROLYSIS PHOTOLYSIS OXIDATION  BIOLYSIS   VOLATILITY TRANSPORT
-------------------------------------------------------------------------
  1L   8.368E-05  5.205E-04  0.000      4.514E-05  1.326E-06  4.200E-02
  2B   6.077E-07  0.000      0.000      1.778E-06  0.000      1.105E-03
  3E   8.573E-05  7.857E-04  0.000      4.598E-06  6.752E-07  1.228E-02
  4H   1.983E-05  1.611E-04  0.000      4.600E-07  0.000      4.163E-03
  5B   1.438E-07  0.000      0.000      9.127E-09  0.000      5.230E-04
  6L   8.368E-05  7.683E-04  0.000      4.514E-06  1.326E-06  4.324E-02
  7B   6.077E-07  0.000      0.000      8.890E-08  0.000      1.105E-03
-------------------------------------------------------------------------
* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC
```

```
EXAMS > LIST 11

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: Methyl Parathion - Baseline.
ECOSYSTEM: OLIGOTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION
-------------------------------------------------------------------------
TABLE 11.  CANONICAL PROFILE OF ECOSYSTEM.
-------------------------------------------------------------------------
CP T*  PH   POH  TEMP REAERATION COMPOSITE BACTERIAL  OXIDANT  DISSOLVED
   Y              DEG.  COEFF.   LIGHT AVE POP. SIZE   CONC.    PERCENT
   P               C.   M/HR         %     CELLS/**   (MOLAR)       %
-------------------------------------------------------------------------
  1L  6.50  7.50 15.0  4.441E-02  43.1      1.000E+03 1.000E-09  98.1
  2B  5.70  8.30 15.0  0.000      0.000     2.000E+05 0.000     0.715
  3E  6.90  7.10 15.0  8.882F-02  59.0       100.     1.000E-09  100.
  4H  7.00  7.00  5.0  0.000      20.3       10.0     5.000E-10  100.
  5B  5.70  8.30  5.0  0.000      0.000     1.000E+03 0.000     0.734
  6L  6.50  7.50 15.0  4.441E-02  59.9       100.     1.000E-09  98.1
  7B  5.70  8.30 15.0  0.000      0.000     1.000E+04 0.000     0.715
-------------------------------------------------------------------------
* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC
** ACTIVE BACTERIAL  POPULATIONS AS CELLS/ML IN WATER COLUMN,
   CELLS/100 G (DRY WEIGHT) OF SEDIMENTS IN BOTTOM SEDIMENTS.
```

```
EXAMS > PRINT ALL

Requested report has been spooled to printer.

EXAMS > PLOT PROF TOT WAT


     0.3600     -I
                 I
                 I
                 I
  C              I LLLLLLLLLLL
T O  0.3200     -I 1         1
O N              I 1         1
T C              I 1         1
A E              I 1         1
L N              I 1         1
  T  0.2800     -I 1         1
M R              I 1         1
G A              I 1         1
/ T              I 1         1
L I              I 1         1 EEEEEEEEEEE
  O  0.2400     -I 1         1 3         3             LLLLLLLLLLL
  N              I 1         1 3         3 HHHHHHHHHHH 6         6
                 I 1         1 3         3 4         4 6         6
                 I 1         1 3         3 4         4 6         6
                 I 1         1 3         3 4         4 6         6
     0.2000     -+_11111111111_33333333333_44444444444_66666666666
                     WATER COLUMN

EXAMS > EXIT
JOB254 -- STOP

00:02:07  Size: 31K  CPU: 58:03  Status: SUCCESS

PDS > LOGOUT
```

3.3.4 Tutorial Session #4: Sample Application Study

Objectives: entry of new chemical and environmental data, exploration of alternative process models. This session duplicates the analysis of volatilization of 1,4-dichlorobenzene discussed in Section 2.3.2.4.2. Note that the environmental data are not a complete canonical description of Lake Zurich; they are restricted to a simple geometry plus those parameters needed to construct volatilization models on EXAMS.

```
PDS > RUN EXAMS
20:27:10
           Welcome to EXAMS
   EXposure Analysis Modeling System
Athens Environmental Research Laboratory
    Released for field trials Jan-81


The ATHENS collection of compounds is available for your use.

EXAMS > COMP IS UNS
Compound selected > Unspecified Chemical

EXAMS > COMP NAME IS 1,4-DICHLOROBENZENE

EXAMS > CHANGE MWT TO 147.0

EXAMS > CHANGE SOL(1) TO 73.8

EXAMS > CH KOW TO 2340

EXAMS > CH HENRY TO 2.66E-3

EXAMS > SHO USER COMP

Directory of user defined compounds

  No. COMPOUND NAME
     3 Methyl Parathion with HIGH biolysis
     4 Methyl Parathion with LOW biolysis.
     7 XXX WITH KPS=100.
     8 XXX WITH KPS=1000.
     9 XXX WITH KPS=10000.

EXAMS > STORE COMP 1

Compound stored > 1,4-DICHLOROBENZENE
```

```
EXAMS > ENV IS UNS
Selected environment is: Unspecified Environment

EXAMS > ENV NAME IS LAKE ZURICH - CENTRAL BASIN (UNTERSEE)

EXAMS > CHA KO2G(1) TO 2.5

EXAMS > CHA WIND TO 1.38

Subscript out-of-range.

EXAMS > HELP WIND
WIND is a REAL VECTOR with 10 rows.
Average wind velocity at a reference height of 10 cm. above the
water surface.  Parameter is used to compute a piston velocity
for water vapor (Liss 1973, Deep-Sea Research 20:221) in
the 2-film treatment of volatilization losses.
Units: meters/second

EXAMS > CH WIND(1) TO 1.38

EXAMS > SHOW KOUNT

KOUNT IS           1

EXAMS > CHANGE KOUNT TO 3

EXAMS > CH TYPE(1) TO E

EXAMS > CH TYPE(2) TO H

EXAMS > CHA TYPE(3) TO B

EXAMS  > CH DEPTH(1) TO 10.

EXAMS > CH VOLG(1) TO 6.8E8

EXAMS > CH DEPTH(2) TO 40

EXAMS > CH VOLG(2) TO 2.72E9

EXAMS > CHA DEPTH(3) TO 0.02

EXAMS > CHA VOLG(3) TO 1.36E6

EXAMS > CHAN AREA(*) TO 6.8E7

EXAMS > CH TCEL(1) TO 11

EXAMS > CH TCEL(2) TO 5.6

EXAMS > CHA TCELG(3) TO 5.6
EXAMS > CH DSP(1) TO 0.2

EXAMS > CH DSP(2) TO 1.E-4

EXAMS > CH XSTURG(*) TO 6.8E7

EXAMS > CH JTUR(1) TO 1

EXAMS > CH ITUR(1) TO 2

EXAMS > CH JTUR(2) TO 2

EXAMS > CH ITUR(2) TO 3

EXAMS > SHO TUR

Environment: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
Compartments (KOUNT):  3
                              1  2  3
Type of compartment (TYPEE):  E  H  B

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DICHLOROBENZENE
ECOSYSTEM: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
------------------------------------------------------------------------
TABLE 8.  INPUT DATA DESCRIBING ENVIRONMENT: TURBULENT INTERCONNECTIONS.

COMP. NO. (JTURB)      1          2
CONNECTED (ITURB)      2          3
X-SECTION (XSTUR)  6.800E+07  6.800E+07
CHAR. LN. (CHARL)   1.00      0.000
EDDY DISP. (DSP)   0.200      1.000E-04


EXAMS > HELP CHARL
CHARL is a REAL VECTOR with 30 rows.
Characteristic length (average of compartment dimensions or mixing
lengths) for the dispersive exchange pairing given by the corresponding
compartment numbers of JTURB and ITURB.  A given compartment may have
different mixing lengths in different exchange pairings.
Units: meters

EXAMS > CHA CHARL(1) TO 25

EXAMS > CHA CHARL(2) TO 20.01
EXAMS > SHO TUR
Environment: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
Compartments (KOUNT):  3
                                1  2  3
Type of compartment (TYPEE):    E  H  B

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DICHLOROBENZENE
ECOSYSTEM: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
-----------------------------------------------------------------------
TABLE 8.  INPUT DATA DESCRIBING ENVIRONMENT: TURBULENT INTERCONNECTIONS.

COMP. NO. (JTURB)       1           2
CONNECTED (ITURB)       2           3
X-SECTION (XSTUR)  6.800E+07  6.800E+07
CHAR. LN. (CHARL)   25.0        20.0
EDDY DISP. (DSP)   0.200      1.000E-04


EXAMS > CHAN SDCHRG(*) TO 5

EXAMS > CH SDCHRG(3) TO 1.5

EXAMS > CH PCTWAG(3) TO 150.

EXAMS > CHAN FROC(*) TO .02

EXAMS > CH STFLG(1) TO 3.E5

Unrecognized variable name.

EXAMS > HELP STFL

STFLO is a REAL VECTOR with 10 rows.
Stream flow entering ecosystem compartments.  Stream flows
include base flow into head reach of river or estuary,
tributaries, creeks entering a lake or pond, etc.
Units: cubic meters/hour

EXAMS > CHAN STFLO(1) TO 3.E5

EXAMS > CHAN STRLD(1) TO 0.01

EXAMS > RUN

Simulation beginning for:
Compound: 1,4-DICHLOROBENZENE
Environment: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
with a load of (kg/hr) >  0.1000000E-01
```

```
HYDROLOGIC DEFINITION OF COMPARTMENT   1 IS IMPROPER.
THERE IS A NET ADVECTED FLOW LEAVING THIS COMPARTMENT,
BUT THE FLOW PATHWAY HAS NOT BEEN SPECIFIED.
SIMULATION ABORTED.

Run complete.

EXAMS > CHANGE JFRAD(1) TO 1

EXAMS > CHA ADVPR(1) TO 1.0

EXAMS > SHO AD

Environment: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
Compartments (KOUNT):  3
                             1  2  3
Type of compartment (TYPEE): E  H  B


  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DICHLOROBENZENE
ECOSYSTEM: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
========================================================================
TABLE 7.  INPUT DATA DESCRIBING ENVIRONMENT: ADVECTIVE INTERCONNECTIONS.
========================================================================
COMP. NO. (JFRAD)     1
CONNECTED (ITOAD)     0
ADVECTION (ADVPR)  1.00

EXAMS > RUN

Simulation beginning for:
Compound: 1,4-DICHLOROBENZENE
Environment: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
with a load of (kg/hr) >  0.1000000E-01

Run complete.

EXAMS > LI 13
```

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DICHLOROBENZENE
ECOSYSTEM: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
-------------------------------------------------------------------------
TABLE 13. DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
-------------------------------------------------------------------------
COMP STEADY-STATE RESIDENT MASS     **** TOXICANT CONCENTRATIONS ****
        2                             TOTAL   DISSOLVED SEDIMENTS   BIOTA
     G/M        KILOS          %      MG/*      MG/L      MG/KG      UG/G
--- ------     ------     ------  --------- --------- --------- ---------
  1 1.074E-04  7.302       20.00  1.074E-05 1.074E-05 2.060E-04 0.000
  2 4.295E-04  29.21       80.00  1.074E-05 1.074E-05 2.060E-04 0.000
 SUBTOTAL:     36.51       99.22
 AND IN THE BOTTOM SEDIMENTS:
  3 4.228E-06 0.2875      100.00  2.114E-04 1.074E-05 2.060E-04 0.000
 SUBTOTAL:    0.2875        0.78
TOTAL MASS (KILOGRAMS) =      36.80
-------------------------------------------------------------------------
* TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.

EXAMS > LI 15

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DICHLOROBENZENE
ECOSYSTEM: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
-------------------------------------------------------------------------
TABLE 15.  ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.
-------------------------------------------------------------------------
               PROCESS                 MASS FLUX    % OF LOAD    HALF-LIFE*
                                        KG/DAY                      DAYS
     ------------------------          ---------    ---------    ---------
     HYDROLYSIS                        0.0000          0.00          ---
     OXIDATION                         0.0000          0.00          ---
     PHOTOLYSIS                        0.0000          0.00          ---
  ALL CHEMICAL PROCESSES               0.0000          0.00          ---
-------------------------------------------------------------------------
     WATER COLUMN (BACTERIA)           0.0000          0.00          ---
     BOTTOM SEDIMENTS (BACTERIA)       0.0000          0.00          ---
  TOTAL BIOLYSIS                       0.0000          0.00          ---
-------------------------------------------------------------------------
     VOLATILIZATION                    0.1627         67.79        156.8
     WATER-BORNE EXPORT                7.7315E-02     32.21        329.9
-------------------------------------------------------------------------
TRANSFORMATION AND TRANSPORT           0.2400        100.00
TOTAL SYSTEM LOAD                      0.2400
RESIDUAL ACCUMULATION RATE:            2.2352E-08      0.00
-------------------------------------------------------------------------
* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.

EXAMS > LI 17
```

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DICHLORDBENZENE
ECOSYSTEM: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
-------------------------------------------------------------------------
TABLE 17.  EXPOSURE ANALYSIS SUMMARY.
-------------------------------------------------------------------------
EXPOSURE:
 A. MAXIMUM CONC. IN WATER COLUMN: 1.07E-05 MG/L DISSOLVED, 1.07E-05 TOT
    MAX. CONC. IN BOTTOM SEDIMENT: 1.07E-05 MG/L DISSOLVED IN PORE WATER
 B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON: 0.00      UG/G
                                       BENTHOS:  0.00      UG/G
 C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS: 2.11E-04 MG/KG (DRY WEIGHT)
FATE:
 A. TOTAL STEADY-STATE ACCUMULATION:  37.     KG; 99.22% IN WATER COL.,
       0.78% IN BOTTOM SEDIMENTS.
 B. TOTAL LOAD: 0.24     KG/DAY - DISPOSITION:   0.00% VIA CHEMICAL
      TRANSFORMATIONS,   0.00% BIOTRANSFORMED,  67.79% VOLATILIZED,
       32.21% EXPORTED VIA OTHER PATHWAYS.
PERSISTENCE:
 A. AT THE END OF A  216.     DAY RECOVERY PERIOD, THE WATER COLUMN HAD
      LOST  50.51% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD
      LOST  19.54% OF THEIR INITIAL BURDEN (  50.26% REMOVAL OVERALL).
 B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY 36. MONTHS.


EXAMS > SHOW USER ENV
Directory of user defined ENVIRONMENTS

  No. ENVIRONMENT NAME
    5 Alkaline Pond - enhanced hydrolysis

EXAMS > STOR ENV 1
Environment stored: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)

EXAMS > PRINT ALL
Requested report has been spooled to printer.

EXAMS > SHO USER ENV

Directory of user defined ENVIRONMENTS
  No. ENVIRONMENT NAME
    1 LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
    5 Alkaline Pond - enhanced hydrolysis

EXAMS > CHA DRFLD(2) TO 1.5E-3

EXAMS > CH STRLD(1) TO 8.5E-3

EXAMS > ENV NAME IS LAKE ZURICH WITH PARTIAL LOAD TO HYPOLIMNION

EXAMS > RUN
```

```
Simulation beginning for:
Compound: 1,4-DICHLOROBENZENE
Environment: LAKE ZURICH WITH PARTIAL LOAD TO HYPOLIMNION
with a load of (kg/hr) >  0.1000000E-01

Run complete.

EXAMS > LI 13


  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DICHLOROBENZENE
ECOSYSTEM: LAKE ZURICH WITH PARTIAL LOAD TO HYPOLIMNION
-------------------------------------------------------------------------
TABLE 13. DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
-------------------------------------------------------------------------
COMP STEADY-STATE RESIDENT MASS     **** TOXICANT CONCENTRATIONS ****
       2                            TOTAL   DISSOLVED SEDIMENTS   BIOTA
     G/M        KILOS        %       MG/*     MG/L      MG/KG      UG/G
--- ------     ------     ------  --------- --------- --------- ---------
  1 1.074E-04  7.302       16.59  1.074E-05 1.074E-05 2.060E-04 0.000
  2 5.398E-04  36.71       83.41  1.350E-05 1.349E-05 2.589E-04 0.000
 SUBTOTAL:     44.01       99.19
 AND IN THE BOTTOM SEDIMENTS:
  3 5.313E-06 0.3613      100.00  2.657E-04 1.349E-05 2.589E-04 0.000
 SUBTOTAL:    0.3613        0.81
TOTAL MASS (KILOGRAMS) =     44.37
-------------------------------------------------------------------------
* TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.

EXAMS > LI 15
```

```
   AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DICHLOROBENZENE
ECOSYSTEM: LAKE ZURICH WITH PARTIAL LOAD TO HYPOLIMNION
-------------------------------------------------------------------------
TABLE 15.  ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.
-------------------------------------------------------------------------
             PROCESS                MASS FLUX    % OF LOAD    HALF-LIFE*
                                     KG/DAY                      DAYS
      -----------------------      ---------    ---------    ---------
      HYDROLYSIS                   0.0000          0.00          ---
      OXIDATION                    0.0000          0.00          ---
      PHOTOLYSIS                   0.0000          0.00          ---
  ALL CHEMICAL PROCESSES           0.0000          0.00          ---
-------------------------------------------------------------------------
      WATER COLUMN (BACTERIA)      0.0000          0.00          ---
      BOTTOM SEDIMENTS (BACTERIA)  0.0000          0.00          ---
  TOTAL BIOLYSIS                   0.0000          0.00          ---
-------------------------------------------------------------------------
      VOLATILIZATION               0.1627         67.79         189.1
      WATER-BORNE EXPORT           7.7315E-02     32.21         397.8
-------------------------------------------------------------------------
TRANSFORMATION AND TRANSPORT       0.2400        100.00
TOTAL SYSTEM LOAD                  0.2400
RESIDUAL ACCUMULATION RATE:        2.2352E-08      0.00
-------------------------------------------------------------------------
* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.

EXAMS > LI 17

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DICHLOROBENZENE
ECOSYSTEM: LAKE ZURICH WITH PARTIAL LOAD TO HYPOLIMNION
-------------------------------------------------------------------------
TABLE 17.  EXPOSURE ANALYSIS SUMMARY.
-------------------------------------------------------------------------
EXPOSURE:
 A. MAXIMUM CONC. IN WATER COLUMN: 1.35E-05 MG/L DISSOLVED, 1.35E-05 TOT
 .   MAX. CONC. IN BOTTOM SEDIMENT: 1.35E-05 MG/L DISSOLVED IN PORE WATER
 B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON: 0.00     UG/G
                                       BENTHOS:  0.00     UG/G
 C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS: 2.66E-04 MG/KG (DRY WEIGHT)
FATE:
 A. TOTAL STEADY-STATE ACCUMULATION:  44.     KG; 99.19% IN WATER COL.,
       0.81% IN BOTTOM SEDIMENTS.
 B. TOTAL LOAD: 0.24     KG/DAY - DISPOSITION:   0.00% VIA CHEMICAL
      TRANSFORMATIONS,   0.00% BIOTRANSFORMED,  67.79% VOLATILIZED,
       32.21% EXPORTED VIA OTHER PATHWAYS.
PERSISTENCE:
 A. AT THE END OF A  252.     DAY RECOVERY PERIOD, THE WATER COLUMN HAD
      LOST  54.35% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD
      LOST  25.70% OF THEIR INITIAL BURDEN (  54.11% REMOVAL OVERALL).
 B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY 37. MONTHS.
```

```
EXAMS > CHA KVOG TO 0.35

EXAMS > COMP NAME IS 1,4-DCB WITH DIFFUSIVITY TRANSPORT INDEX

EXAMS > RECALL ENV 1

Selected environment is: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)

EXAMS > CHAN STRLD(1) TO 0.01

EXAMS > RUN

Simulation beginning for:
Compound: 1,4-DCB WITH DIFFUSIVITY TRANSPORT INDEX
Environment: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
with a load of (kg/hr) >  0.1000000E-01

Run complete.

EXAMS > LI 13


  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DCB WITH DIFFUSIVITY TRANSPORT INDEX
ECOSYSTEM: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
------------------------------------------------------------------------
TABLE 13. DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
------------------------------------------------------------------------
COMP STEADY-STATE RESIDENT MASS     **** TOXICANT CONCENTRATIONS ****
        2                          TOTAL   DISSOLVED SEDIMENTS   BIOTA
     G/M       KILOS        %       MG/*     MG/L      MG/KG      UG/G
--- ------    ------     ------   --------- --------- --------- ---------
  1 1.290E-04  8.771      20.00   1.290E-05 1.290E-05 2.475E-04 0.000
  2 5.159E-04  35.08      80.00   1.290E-05 1.290E-05 2.475E-04 0.000
 SUBTOTAL:     43.85      99.22
 AND IN THE BOTTOM SEDIMENTS:
  3 5.078E-06 0.3453     100.00   2.539E-04 1.290E-05 2.475E-04 0.000
 SUBTOTAL:     0.3453      0.78
TOTAL MASS (KILOGRAMS) =     44.20
------------------------------------------------------------------------
* TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.

EXAMS > LI 15
```

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DCB WITH DIFFUSIVITY TRANSPORT INDEX
ECOSYSTEM: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
-------------------------------------------------------------------------
TABLE 15.  ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.
-------------------------------------------------------------------------
             PROCESS                 MASS FLUX   % OF LOAD   HALF-LIFE*
                                      KG/DAY                    DAYS
      ------------------------       ---------   ---------   ---------
      HYDROLYSIS                     0.0000         0.00        ---
      OXIDATION                      0.0000         0.00        ---
      PHOTOLYSIS                     0.0000         0.00        ---
  ALL CHEMICAL PROCESSES             0.0000         0.00        ---
-------------------------------------------------------------------------
      WATER COLUMN (BACTERIA)        0.0000         0.00        ---
      BOTTOM SEDIMENTS (BACTERIA)    0.0000         0.00        ---
  TOTAL BIOLYSIS                     0.0000         0.00        ---
-------------------------------------------------------------------------
      VOLATILIZATION                 0.1471        61.30       208.2
      WATER-BORNE EXPORT             9.2869E-02    38.70       329.9
-------------------------------------------------------------------------
TRANSFORMATION AND TRANSPORT         0.2400       100.00
TOTAL SYSTEM LOAD                    0.2400
RESIDUAL ACCUMULATION RATE:          2.2352E-08     0.00
-------------------------------------------------------------------------
* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.

EXAMS > CH KVOG TO 0.59

EXAMS > COMP NAME IS 1,4-DCB WITH SQRT(DIFFUSIVITY) TRANSPORT INDEX

EXAMS > RUN

Simulation beginning for:
Compound: 1,4-DCB WITH SQRT(DIFFUSIVITY) TRANSPORT INDEX
Environment: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
with a load of (kg/hr) >  0.1000000E-01

Run complete.

EXAMS > LIST 13
```

```
   AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
 CHEMICAL: 1,4-DCB WITH SQRT(DIFFUSIVITY) TRANSPORT INDEX
 ECOSYSTEM: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
 -------------------------------------------------------------------------
 TABLE 13. DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
 -------------------------------------------------------------------------
 COMP STEADY-STATE RESIDENT MASS      **** TOXICANT CONCENTRATIONS ****
         2                              TOTAL   DISSOLVED SEDIMENTS    BIOTA
      G/M        KILOS         %        MG/*      MG/L      MG/KG      UG/G
 --- -------     ------     ------ --------- --------- --------- ---------
   1 9.131E-05  6.209        20.00  9.131E-06 9.130E-06 1.752E-04 0.000
   2 3.652E-04  24.84        80.00  9.131E-06 9.130E-06 1.752E-04 0.000
  SUBTOTAL:     31.05        99.22
  AND IN THE BOTTOM SEDIMENTS:
   3 3.595E-06 0.2445       100.00  1.798E-04 9.130E-06 1.752E-04 0.000
  SUBTOTAL:    0.2445         0.78
 TOTAL MASS (KILOGRAMS) =       31.29
 -------------------------------------------------------------------------
 * TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.

 EXAMS > LI 15

   AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
 CHEMICAL: 1,4-DCB WITH SQRT(DIFFUSIVITY) TRANSPORT INDEX
 ECOSYSTEM: LAKE ZURICH - CENTRAL BASIN (UNTERSEE)
 -------------------------------------------------------------------------
 TABLE 15.  ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.
 -------------------------------------------------------------------------
                  PROCESS                 MASS FLUX    % OF LOAD    HALF-LIFE*
                                           KG/DAY                      DAYS
      -------------------------         ---------    ---------    ---------
      HYDROLYSIS                         0.0000         0.00          ---
      OXIDATION                          0.0000         0.00          ---
      PHOTOLYSIS                         0.0000         0.00          ---
   ALL CHEMICAL PROCESSES                0.0000         0.00          ---
 -------------------------------------------------------------------------
      WATER COLUMN (BACTERIA)            0.0000         0.00          ---
      BOTTOM SEDIMENTS (BACTERIA)        0.0000         0.00          ---
   TOTAL BIOLYSIS                        0.0000         0.00          ---
 -------------------------------------------------------------------------
      VOLATILIZATION                     0.1743        72.61         124.5
      WATER-BORNE EXPORT                 6.5743E-02    27.39         329.9
 -------------------------------------------------------------------------
 TRANSFORMATION AND TRANSPORT            0.2400       100.00
 TOTAL SYSTEM LOAD                       0.2400
 RESIDUAL ACCUMULATION RATE:             0.0000         0.00
 -------------------------------------------------------------------------
 * HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.
```

```
EXAMS > SHOW USER COMP

Directory of user defined compounds

  No. COMPOUND NAME
    1 1,4-DICHLOROBENZENE
    3 Methyl Parathion with HIGH biolysis
    4 Methyl Parathion with LOW biolysis.
    7 XXX WITH KPS=100.
    8 XXX WITH KPS=1000.
    9 XXX WITH KPS=10000.

EXAMS > RECALL COMP 1
Compound selected > 1,4-DICHLOROBENZENE

EXAMS > ENV NAME IS LAKE ZURICH WITH OCEANIC WIND AND REAERATION

EXAMS > SHOW KO2(1)

KO2 IS   2.700

EXAMS > CHANGE KO2(1) TO 20.

EXAMS > SHOW WIND(1)

WIND IS   1.600

EXAMS > CHANGE WIND(1) TO 2.6245

EXAMS > RUN

No load specified.
Simulation not performed.

EXAMS > CHA STRLD(1) TO 0.01

EXAMS > RUN

Simulation beginning for:
Compound: 1,4-DICHLOROBENZENE
Environment: LAKE ZURICH WITH OCEANIC WIND AND REAERATION
with a load of (kg/hr) >  0.1000000E-01

Run complete.

EXAMS > LIST 13
```

```
  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DICHLOROBENZENE
ECOSYSTEM: LAKE ZURICH WITH OCEANIC WIND AND REAERATION
---------------------------------------------------------------------------
DISTRIBUTION OF ORGANIC TOXICANT AT STEADY-STATE:  IN THE WATER COLUMN:
---------------------------------------------------------------------------
COMP STEADY-STATE RESIDENT MASS    **** TOXICANT CONCENTRATIONS ****
        2                             TOTAL    DISSOLVED SEDIMENTS   BIOTA
     G/M          KILOS        %      MG/*      MG/L      MG/KG      UG/G
--- ------      ------      ------ --------- --------- --------- ---------
  1 1.952E-05   1.328       20.00  1.952E-06 1.952E-06 3.746E-05 0.000
  2 7.810E-05   5.311       80.00  1.952E-06 1.952E-06 3.746E-05 0.000
 SUBTOTAL:      6.638       99.22
 AND IN THE BOTTOM SEDIMENTS:
  3 7.687E-07 5.2273E-02 100.00    3.844E-05 1.952E-06 3.746E-05 0.000
 SUBTOTAL:      5.2273E-02   0.78
TOTAL MASS (KILOGRAMS) =      6.691
---------------------------------------------------------------------------
* TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.

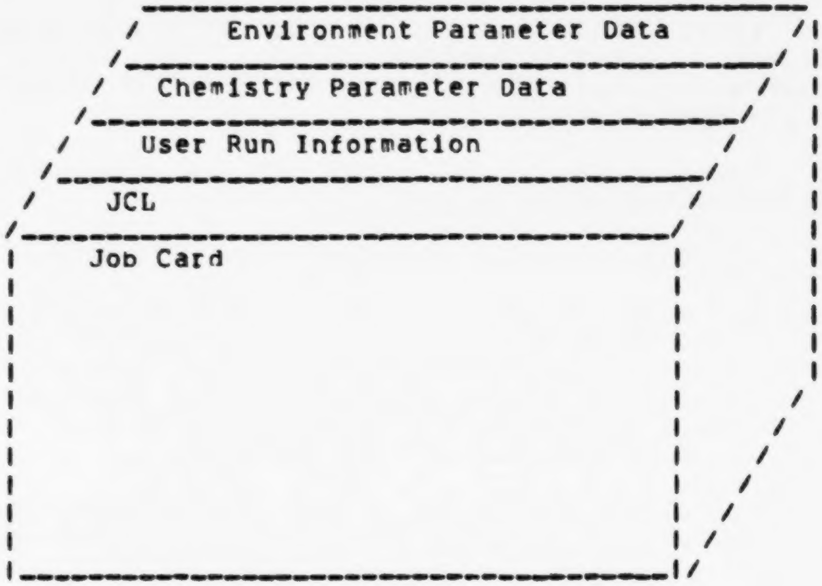
EXAMS > LIST 15

  AERL-ESB MODEL OF FATE OF ORGANIC TOXICANTS IN AQUATIC ECOSYSTEMS
CHEMICAL: 1,4-DICHLOROBENZENE
ECOSYSTEM: LAKE ZURICH WITH OCEANIC WIND AND REAERATION
---------------------------------------------------------------------------
         ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT
---------------------------------------------------------------------------
              PROCESS                  MASS FLUX    % OF LOAD   HALF-LIFE*
                                        KG/DAY                     DAYS
     ------------------------         ---------    ---------   ---------
     HYDROLYSIS                        0.0000          0.00        ---
     OXIDATION                         0.0000          0.00        ---
     PHOTOLYSIS                        0.0000          0.00        ---
 ALL CHEMICAL PROCESSES                0.0000          0.00        ---
---------------------------------------------------------------------------
     WATER COLUMN (BACTERIA)           0.0000          0.00        ---
     BOTTOM SEDIMENTS (BACTERIA)       0.0000          0.00        ---
 TOTAL BIOLYSIS                        0.0000          0.00        ---
---------------------------------------------------------------------------
     VOLATILIZATION                    0.2259         94.14      20.53
     WATER-BORNE EXPORT                1.4058E-02      5.86      329.9
---------------------------------------------------------------------------
TRANSFORMATION AND TRANSPORT           0.2400        100.00
TOTAL SYSTEM LOAD                      0.2400
RESIDUAL ACCUMULATION RATE:            0.0000          0.00
---------------------------------------------------------------------------
* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.

EXAMS > QUIT
JOB104 -- STOP
20:44:10  Size: 31K  CPU: 1:9.78  Status: SUCCESS
```

3.4 Preparing Batch Input Data

EXAMS' batch input data are arranged as diagramed below. The input stream includes three data sets: user run information, chemical parameters, and environmental parameters.


Environment Parameter Data
Chemistry Parameter Data
User Run Information
JCL
Job Card

This Section contains four subsections:

3.4.1 Format Codes

3.4.2 Creating or Changing the User Run Information

3.4.3 Creating or Changing the Chemical Data

3.4.4 Creating or Changing the Environmental Data

Section 3.4.1 is a detailed list of format codes. Sections 3.4.2, 3.4.3, and 3.4.4 describe the parameters for user run information, chemical data and environmental data, respectively. Figures 3.1, 3.2, and 3.3 are sample data sets with parameter names and format codes.

To make a change in the input data, locate the parameter in the parameter index, Table 3.1. On the indicated page, find the description of the parameter to be changed and its format code. The format code refers to the detailed description of the parameter layout in Section 3.4.1. The sample data sets in Figures 3.1, 3.2, and 3.3 show the relative position and sequence of the parameters.

For example, to change the pH of compartment #5 in the environmental data:

1. The parameter index refers PHG to page 249.
2. Page 249 defines the parameter and gives its format code as "5."
3. In Section 3.4.1, format code 5 describes records as "8F10.0." This field width must be preserved when the data base is altered.
4. Locate PHG in the sample environmental data input (Figure 3.3) for the relative position of the parameter in the input data stream.

To create an entirely new set of input data, all parameters must be present as described in Sections 3.4.2, 3.4.3, and 3.4.4.

Table 3.1 Parameter Index

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KAHG	242,244,246
KBACSG	243,245,246
KBACWG	243,245,246
KBHG	243,245,246
KCECG	244
KDPG	242,244,246
KNHG	242,244,246
KO2G	249
KOCG	241
KOUNT	247
KOWG	241
KOXG	243,245,246
KPBG	241,244,245
KPSG	241,244,245
KVOG	241
LAMAXG	242
LATG	247
MWTG	241
NLOAD	240
NPSEDG	247
NPSFLG	247
NPSLDG	240
NSPEC1	248
NSPEC2	248
OXRADG	249
PCPLDG	240
PCTWAG	248
PHG	249
PKAG	245
PKBG	243
PLRAG	249
POHG	249
QTBASG	243,245,246
QTBAWG	243,245,246
QUANTG	242,244,245
RAING	248
RFLATG	242,244,246
SDCHRG	248
SOLG	241,243,245
SPFLG	241
STFLOG	247
STRLDG	240
STSEDG	247
SYSTYP	247
TCELG	249
TYPEE	247
VAPRG	241
VOLG	247
WINDG	247
WLAMG	248
XSTURG	249

```
BFQ                                                     ...CHEM1
EUL                                                     ...ECO2
    5                                                   ...NLOAD
    1 0.500         0.16 6.4000E-03        0.        0. ... *
    2        0.        0.        0.        0.      0.02 ... *
    3        0.        0.    0.0320        0.        0. ... *
    6        0.      0.166.4000E-03        0.        0. ... *
    7        0.        0.        0.        0. 2.000E-02 ... *
```

* I, STRLDG(I), NPSLDG(I), PCPLDG(I), DRFLDG(I), IFLLDG(I)

Figure 3.1 Sample user run input.

```
BFQ                                                                             ... CHEM2
BENZO[f]QUINOLINE                                                               ... CHEMNA 1
1 1 0 0 0                                                                       ... SPFLG 8
 179.2     76.10     0.000                                                      ... MWTG,SOLG(1),ESOLG(1) 9
 1300.     500.0    0.0000    0.0000                                            ... KPSG(1),KPBG(1),KOCG,KOWG 10
0.2200E-030.0000    0.0000    0.2800E-040.0000                                  ... KVOG,HENRYG,EHENG,VAPRG,EVPRG 10
0.1400E-010.0000    0.0000                                                      ... QUANTG(1,1),QUANTG(2,1),QUANTG(3,1) 9
 3984.     3910.     2056.     1380.     1120.     1048.     1310.     1586.    ... ABS1 (RECORD 1) 6
 1396.     1332.     1454.     3008.     1584.     1350.     57.00     15.60    ... ABS1 (RECORD 2)
 16.70    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    ... ABS1 (RECORD 3)
0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    ... ABS1 (RECORD 4)
0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000              ... ABS1 (RECORD 5)
0.0000     40.00      298.                                                      ... KDPG(1),RFLATG(1),LAMAXG 11
0.0000    0.0000    0.0000                                                      ... KAHG(1,1),KAHG(2,1),KAHG(3,1) 9
0.0000    0.0000    0.0000                                                      ... EAHG(1,1),EAHG(2,1),EAHG(3,1) 9
0.0000    0.0000    0.0000                                                      ... KNHG(1,1),KNHG(2,1),KNHG(3,1) 9
0.0000    0.0000    0.0000                                                      ... ENHG(1,1),ENHG(2,1),ENHG(3,1) 9
0.0000    0.0000    0.0000                                                      ... KBHG(1,1),KBHG(2,1),KBHG(3,1) 9
0.0000    0.0000    0.0000                                                      ... EBHG(1,1),EBHG(2,1),EBHG(3,1) 9
0.0000    0.0000    0.0000                                                      ... KOXG(1,1),KOXG(2,1),KOXG(3,1) 9
0.0000    0.0000    0.0000                                                      ... EOXG(1,1),EOXG(2,1),EOXG(3,1) 9
0.3600E-070.0000    0.0000                                                      ... KBACWG(1,1),KBACWG(2,1),KBACWG(3,1) 9
 2.000    0.0000    0.0000                                                      ... QTBAWG(1,1),QTBAWG(2,1),QTBAWG(3,1) 9
0.3600E-070.0000    0.0000                                                      ... KBACSG(1,1),KBACSG(2,1),KBACSG(3,1) 9
 2.000    0.0000    0.0000                                                      ... QTBASG(1,1),QTBASG(2,1),QTBASG(3,1) 9
 8.850    0.0000     761.0    0.0000                                            ... PKBG(1),EPKBG(1),SOLG(2),ESOLG(2) 10
 130.0     50.00    0.0000                                                      ... KPSG(2),KPBG(2),KCECG(2) 9
0.1400E-010.0000    0.0000                                                      ... QUANTG(1,2),QUANTG(2,2),QUANTG(3,2) 9
 3621.     3910.     3328.     3197.     2937.     3047.     3127.     2858.    ... ABS2 (RECORD 1) 6
 2668.     2059.     1999.     3190.     3038.     4076.     2983.     2578.    ... ABS2 (RECORD 2)
 1216.     665.0    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    ... ABS2 (RECORD 3)
0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    ... ABS2 (RECORD 4)
0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000              ... ABS2 (RECORD 5)
0.0000     40.00                                                                ... KDPG(2),RFLATG(2) 11
0.0000    0.0000    0.0000                                                      ... KAHG(1,2),KAHG(2,2),KAHG(3,2) 9
0.0000    0.0000    0.0000                                                      ... EAHG(1,2),EAHG(2,2),EAHG(3,2) 9
0.0000    0.0000    0.0000                                                      ... KNHG(1,2),KNHG(2,2),KNHG(3,2) 9
0.0000    0.0000    0.0000                                                      ... ENHG(1,2),ENHG(2,2),ENHG(3,2) 9
0.0000    0.0000    0.0000                                                      ... KBHG(1,2),KBHG(2,2),KBHG(3,2) 9
0.0000    0.0000    0.0000                                                      ... EBHG(1,2),EBHG(2,2),EBHG(3,2) 9
0.0000    0.0000    0.0000                                                      ... KOXG(1,2),KOXG(2,2),KOXG(3,2) 9
0.0000    0.0000    0.0000                                                      ... EOXG(1,2),EOXG(2,2),EOXG(3,2) 9
0.3600E-070.0000    0.0000                                                      ... KBACWG(1,2),KBACWG(2,2),KBACWG(3,2) 9
 2.000    0.0000    0.0000                                                      ... QTBAWG(1,2),QTBAWG(2,2),QTBAWG(3,2) 9
0.3600E-070.0000    0.0000                                                      ... KBACSG(1,2),KBACSG(2,2),KBACSG(3,2) 9
 2.000    0.0000    0.0000                                                      ... QTBASG(1,2),QTBASG(2,2),QTBASG(3,2) 9
```

FIGURE 3.2. SAMPLE CHEMISTRY DATA INPUT

```
EUL                                                                             ...ECO2
EUTROPHIC LAKE, AERL DEVELOPMENT PHASE TEST DEFINITION                          ...SYSTYP 1
    7                                                                           ...KOUNT 2
L                                                                               ...TYPEE (RECORD 1) 3
B                                                                               ...TYPEE (RECORD 2)
E                                                                               ...TYPEE (RECORD 3)
H                                                                               ...TYPEE (RECORD 4)
B                                                                               ...TYPEE (RECORD 5)
L                                                                               ...TYPEE (RECORD 6)
B                                                                               ...TYPEE (RECORD 7)
 40.00                                                                          ...LATG 4
 1.500    0.0000     2.000    0.0000    0.0000     1.500    0.0000              ...WINDG 5
0.2500E+06 2500.    0.2500E+070.2500E+070.1250E+050.2500E+06 2500.              ...VOLG 5
0.5000E+050.5000E+050.2500E+060.2500E+060.2500E+060.5000E+050.5000E+05          ...AREAG 5
 5.000    0.5000E-01 10.00     10.00    0.5000E-01 5.000    0.5000E-01          ...DEPTHG 5
 485.0    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000              ...STFLOG 5
 40.00    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000              ...STSEDG 5
 48.50    0.0000    0.0000    0.0000    0.0000     48.50    0.0000              ...NPSFLG 5
 97.00    0.0000    0.0000    0.0000    0.0000     97.00    0.0000              ...NPSEDG 5
0.0000     130.0    0.0000    0.0000     130.0    0.0000     130.0              ...INTFLG 5
 105.0                                                                          ...RAING 4
 5.000                                                                          ...CLOUDG 4
0.8910E+110.3380E+120.1110E+130.2990E+130.5400E+130.8840E+130.1380E+140.1850E+14...WLAMG (RECORD 1) 6
0.2330E+140.2810E+140.5210E+140.1810E+150.2110E+150.2260E+150.2410E+150.2680E+15...WLAMG (RECORD 2)
0.2940E+150.3660E+150.5260E+150.6920E+150.7120E+150.6880E+150.8140E+150.9170E+15...WLAMG (RECORD 3)
0.9270E+150.9590E+150.9830E+150.9300E+150.9490E+150.1000E+160.1050E+160.1060E+16...WLAMG (RECORD 4)
0.1070E+160.1080E+160.1080E+160.1080E+160.1070E+160.1030E+160.9880E+15          ...WLAMG (RECORD 5)
 1.190    0.0000     1.190     1.190    0.0000     1.190    0.0000              ...DFACG 5
 90.00    0.0000     85.00    0.0000    0.0000     90.00    0.0000              ...EVAPG 5
0.5000     1.850    0.5000    0.5000     1.850    0.5000     1.850              ...SDCHRG 5
0.0000     137.0    0.0000    0.0000     137.0    0.0000     137.0              ...PCTWAG 5
    7                                                                           ...NSPEC1 2
    1    3    6    2    5    7    4                                             ...JFRADG (RECORD 1) 7
    3    6    0    1    4    6    3                                             ...ITOADG (RECORD 1) 7
 1.000     1.000     1.000     1.000     1.000     1.000     1.0000             ...ADVPRG (RECORD 1) 12
    6                                                                           ...NSPEC2 2
    1    3    4    6    1    3                                                  ...JTURBG (RECORD 1) 7
    2    4    5    7    3    6                                                  ...ITURBG (RECORD 1) 7
0.5000E+050.2500E+060.2500E+060.5000E+05 2500.     2500.                        ...XSTURG (RECORD 1) 12
 2.525     10.00     5.025     2.525     300.0     300.0                        ...CHARLG (RECORD 1) 12
0.4676E-040.3985    0.9306E-040.4676E-04 1196.     1196.                        ...DSPG (RECORD 1) 12
0.3800E-010.3800E-010.3800E-010.3800E-010.3800E-010.3800E-010.3800E-01          ...FROCG 5
 25.00     25.00     25.00     25.00     25.00     25.00     25.00              ...CECG 5
 25.00     25.00     25.00     25.00     25.00     25.00     25.00              ...AKCG 5
 20.00     20.00     20.00     5.000     5.000     20.00     20.00              ...TCELG 5
 8.000     6.500     8.000     7.400     6.500     8.000     6.500              ...PHG 5
 6.000     7.500     6.000     6.600     7.500     6.000     7.500              ...POHG 5
0.1000E-08 0.000    0.1000E-080.5000E-09 0.000    0.1000E-08 0.000              ...OXRADG 5
 51.00     250.0     2.200     0.7500    10.00     51.00     250.0              ...BIOMSG 5
0.2000E-010.0000     1.000     1.000    0.0000    0.2000E-010.0000              ...PLRAG 5
 20.00      20.00    20.00     5.000     5.000     20.00     20.00              ...BIOTMG 5
0.1000E+060.2000E+080.1000E+050.1000E+040.2000E+070.1000E+070.2000E+08          ...BACTOG 5
 1.000     1.000     1.000     1.000     1.000     1.000     1.000              ...ACBACG 5
 5.000    0.0000     10.00    0.0000    0.0000     5.000    0.0000              ...KO2G 5
 2.000    0.0000     2.000     1.000    0.0000     2.000    0.0000              ...CHPETG 5
 2.500    0.0000     2.500    0.5000    0.0000     2.500    0.0000              ...DOCG 5
0.4000E-020.0000    0.4000E-020.5000E-030.0000    0.4000E-020.0000              ...CHLG 5
```

FIGURE 3.3. SAMPLE ENVIRONMENT DATA INPUT

3.4.1 Format Codes

In the example datasets, Figures 3.2 and 3.3, following the '...' (columns 81-83) are the variable name, record number for that format (if applicable), and format code. The narrative associated with each database also references the format codes.

Code	Format
1	60 characters, left justified. Format: (60A1)
2	Columns 1-5 right justified. Format: (2015)
3	Column 1, one character/record. The maximum number of records is equal to the number of compartments. Format: (A1)
4	Columns 1-10. Format: (F10.0)
5	Each record contains 8 10-column fields, maximum 2 records per variable. Format: (8F10.0)

	Columns	Compartment
Record 1	1-10	1
	11-20	2
	.	.
	.	.
	.	.
Record 2	1-10	9
(if needed)	11-20	10

Code	Format
6	Five record layout containing 39 values. Four records contain eight 10-column fields; the fifth contains seven. Format: (8F10.0)

	Columns	Value
Record 1	1-10	1
	11-20	2
	.	.
	.	.
	.	.
	71-80	8
Record 2	1-10	9
	.	.
	.	.
	.	.
	71-80	16
.		
.		
.		

Record 5	1-10	33
	.	.
	.	.
	.	.
	61-70	39

7 The number of records is equal to NSPEC1 or NSPEC2 divided by 16. Each record contains 16 five column fields. For JFRADG and ITOADG use NSPEC1 and for JTURBG and ITURBG use NSPEC2. Each field is right justified.
Format: (20I5)

	Columns	<Par>
Record 1	1-5	1
	6-10	2
	.	.
	.	.
	.	.
	76-80	16
Record 2	1-5	17
	.	.
	.	.
	.	.
Record n	41-50	29
	51-60	30

8 Format: (5(I1,1X))

Column	Flag
1	1
3	2
5	3
7	4
9	5

9 Format: (8F10.0)

Columns	Value
1-10	1
11-20	2
21-30	3

10 Format: (8F10.0)

Columns	Value
1-10	1
11-20	2
21-30	3
31-40	4

11 Format: (8F10.0)

Columns	Value
1-10	1
11-20	2

12 The number of records is equal to NSPEC1 or NSPEC2 divided by eight. Each record contains eight 10-column fields. For ADVPRG use NSPEC1 and for XSTURG, CHARLG, and DSPG use NSPEC2. Format: (8F10.0)

	Columns	Value
Record 1	1-10	1
	11-20	2
	.	.
	.	.
	.	.
	71-80	8
Record 2	.	.
.	.	.
.	.	.
.	.	.
Record n	41-50	29
	51-60	30

3.4.2 Creating or Changing the User Run Information

This sequential file contains chemical name, ecosystem name, and loads.

Record 1: (CHEM1) Chemical name - three characters maximum.
Format: (A3)

Record 2: (ECO1) Ecosystem name - three characters maximum.
Format: (A3)

Record 3: (NLOAD) Number of loadings.
Format: (I5)

Record 4,...,NLOAD+3: (I,STRLDG,NPSLDG,PCPLDG,DRFLDG,IFLLDG)
Each of NLOAD records contain the load number and the Ith STRLDG, NPSLDG, PCPLDG, DRFLDG, IFLLDG.
Format: (I5,5F10.0)

STRLDG - Stream loadings.
NPSLDG - Non-point source loadings.
PCPLDG - Precipitation loadings.
DRFLDG - Drift loadings.
IFLLDG - Interflow loadings.

	Columns	Field
Record 4	1-5	I
	6-15	STRLDG(I)
	16-25	NPSLDG(I)
	26-35	PCPLDG(I)
	36-45	DRFLDG(I)
	46-55	IFLLDG(I)

3.4.3 Creating or Changing the Chemical Data

Locate the CHEM2 record in the chemistry data. This record acts as a header/delimiter for the associated parameters. The chemical parameter data are located in the following sequential record layout. (The format code list provides the detailed format specifications.)

Record: (CHEMNA) Chemical name. Format: 1

Record: (SPFLG) Flags denoting which species occur. Five flags: 1 denoting occurrence, 0 denoting nonexistence. Format: 8

------------------If SPFLG(1)=1;-----------------------------

Record: (MWTG,SOLG(1),ESOLG(1))
Molecular weight of the toxicant, aqueous solubility of the toxicant chemical species, and exponential term for describing solubility of the toxicant as a function of temperature. Three values per record. Format: 9

Record: (KPSG(1),KPBG(1),KOCG,KOWG)
Partition coefficient of toxicant on compartment sediment. Partition coefficient of toxicant on compartment biomass (BIOMSG). Multiplication of KOCG by the fractional organic carbon content (FROCG(J)) of each system sediment yields the partition coefficient. Octanol-water partition coefficient of toxicant. Four values per record. Format: 10

Record: (KVOG,HENRYG,EHENG,VAPRG,EVPRG)
Measured experimental value for (volatilization) liquid-phase transport resistance, expressed as a ratio to the reaeration rate. Henry's Law constant of the toxicant. Used to compute Henry's Law constant as a function of temperature. Used to compute Henry's Law constant if the latter input datum (HENRYG) is zero, but VAPRG is non-zero. Molar heat of vaporization for vapor pressure described as a function of temperature. Five values per record. Format: 10

Record: (QUANTG(1,1),QUANTG(2,1),QUANTG(3,1))
Reaction quantum yield in photolytic transformation of toxicant. Separate values are provided for each molecular configuration of the toxicant. Three values per record. Format: 9

Record: (ABS1) Absorption spectrum for uncharged molecule (SH2). The following list explains the correspondence between array element and wavelength: 1:297.5, 2:300.0, 3:302.5, 4:305.0, 5:307.5, 6:310.0, 7:312.5, 8:315.0, 9:317.5, 10:320.0, 11:323.1, 12:330.0, 13:340.0, 14:350.0, 15:360.0, 16:370.0, 17:380.0, 18:390.0, 19:400.0, 20:410.0, 21:420.0, 22:430.0, 23:440.0, 24:450.0, 25:460.0, 26:470.0, 27:480.0, 28:490.0, 29:503.75, 30:525.0, 31:550.0, 32:575.0, 33:600.0, 34:625.0, 35:650.0, 36:675.0, 37:706.25, 38:750.0, 39:800.0. Format: 6

Record: (KDPG(1),RFLATG(1),LAMAXG)
A near-surface photolytic rate constant for the Kth chemical species of the toxicant. Reference latitude for corresponding direct photolysis rate constant (c.f. KDPG). Wavelength for computing zenith light extinction coefficient. Three values per record. Format: 11

Record: (KAHG(1,1)KAHG(2,1),KAHG(3,1))
Second-order rate constants for specific-acid catalyzed hydrolysis of toxicant. Three values per record. Format: 9

Record: (EAHG(1,1),EAHG(2,1),EAHG(3,1))
Arrhenius activation energy of specific-acid catalyzed hydrolysis of the toxicant. Matrix indices allow entry of the data as separate value for each chemical species/physical form configuration of the toxicant molecule. Three values per record. Format: 9

Record: (KNHG(1,1),KNHG(2,1),KNHG(3,1))
Rate constants for neutral hydrolysis of organic toxicant. Three values per record. Format: 9

Record: (ENHG(1,1),ENHG(2,1),ENHG(3,1))
Arrhenius activation energy of neutral

hydrolysis of the toxicant. Three values per record. Format: 9

Record: (KBHG(1,1),KBHG(2,1),KBHG(3,1))
Second-order rate constants for specific-base catalyzed hydrolysis of toxicant. Three values per record. Format: 9

Record: (EBHG(1,1),EBHG(2,1),EBHG(3,1))
Arrhenius activation energy of specific-base catalyzed hydrolysis of the toxicant. Three values per record. Format: 9

Record: (KOXG(1,1),KOXG(2,1),KOXG(3,1))
Second-order rate constants for oxidative transformation of toxicant. Three values per record. Format: 9

Record: (EOXG(1,1),EOXG(2,1),EOXG(3,1))
Arrhenius activation energy of oxidative transformation of the toxicant. Three values per record. Format: 9

Record: (KBACWG(1,1),KBACWG(2,1),KBACWG(3,1))
Second-order rate constants for water column bacterial biolysis of the organic toxicant. Three values per record. Format: 9

Record: (QTBAWG(1,1),QTBAWG(2,1),QTBAWG(3,1))
Q-10 Values for bacterial transformation (c.f. KBACWG) of toxicant in water column of the system. Three values per record. Format: 9

Record: (KBACSG(1,1),KBACSG(2,1),KBACSG(3,1))
Second-order rate constants for benthic sediment bacterial biolysis of the organic toxicant. Three values per record. Format: 9

Record: (QTBASG(1,1),QTBASG(2,1),QTBASG(3,1))
Q-10 Values for bacterial transformation (c.f. KBACSG) of organic toxicant in benthic sediments. Three values per record. Format: 9.

------------------If SPFLG(2),SPFLG(3);K=2,3-----------------

Record: (PKBG(1),EPKBG(1),SOLG(K),ESOLG(K))
Negative base-10 logarithm of first (K=2) and second (K=3) base dissociation constants

of organic toxicant. Exponential term for base dissociation constant of toxicant (Kb) as a function of temperature. Aqueous solubility of toxicant chemical species. Exponential term for decribing solubility of the toxicant as a function of temperature. Four values per record. Format: 10

Record: (KPSG(K),KPBG(K),KCECG(K-1))
Partition coefficient of toxicant on compartment sediment. Partition coefficient of toxicant compartment biomass (BIOMSG). Multiplication of the cation exchange capacity of system sediments by KCECG gives the partition coefficient for sorption of the SH3+ cation (KCECG(1)). Three values per record. Format: 9

Record: (QUANTG(1,K),QUANTG(2,K),QUANTG(3,K))
Reaction quantum yield in photolytic transformation of toxicant. Separate values are provided for each molecular configuration of the toxicant. Three values per record. Format: 9

Record: (ABS2) Absorption spectrum for singly charged cation (SH3+). See ABS1. Format: 6

Record: (KDPG(K),RFLATG(K))
A near-surface photolytic rate constant for the Kth chemical species of the toxicant. Reference latitude for corresponding direct photolysis rate constant (c.f. KDPG). Two values per record. Format: 11

Record: (KAHG(1,K),KAHG(2,K),KAHG(3,K))
Second-order rate constants for specific-acid catalyzed hydrolysis of toxicant. Three values per record. Format: 9

Record: (EAHG(1,K),EAHG(2,K),EAHG(3,K))
Arrhenius activation energy of specific-acid catalyzed hydrolysis of the toxicant. Matrix indices allow entry of the data as a separate value for each chemical species/physical form configuration of the toxicant molecule. Three values per record. Format: 9

Record: (KNHG(1,K),KNHG(2,K),KNHG(3,K))
Same as SPFLG(1)

Record: (ENHG(1,K),ENHG(2,K),ENHG(3,K))
Same as SPFLG(1)

Record: (KBHG(1,K),KBHG(2,K),KBHG(3,K))
Same as SPFLG(1)

Record: (EBHG(1,K),EBHG(2,K),EBHG(3,K))
Same as SPFLG(1)

Record: (KOXG(1,K),KOXG(2,K),KOXG(3,K))
Same as SPFLG(1)

Record: (EOXG(1,K),EOXG(2,K),EOXG(3,K))
Same as SPFLG(1)

Record: (KBACWG(1,K),KBACWG(2,K),KBACWG(3,K))
Same as SPFLG(1)

Record: (QTBAWG(1,K),QTBAWG(2,K),QTBAWG(3,K))
Same as SPFLG(1)

Record: (KBACSG(1,K),KBACSG(2,K),KBACSG(3,K))
Same as SPFLG(1)

Record: (QTBASG(1,K),QTBASG(2,K),QTBASG(3,K))
Same as SPFLG(1)

------------------If SPFLG(4),SPFLG(5);L=4,5----------------

Record: (PKAG(1),EPKAG(1),SOLG(L),ESOLG(L))
Negative base-10 logarithm of first (L=4) and second (L=5) acidity constant of organic toxicant. Exponential term for acid dissociation constant of toxicant (Ka). Aqueous solubility of toxicant chemical species. Exponential term for describing solubility of the toxicant as a function of temperature. Four values per record. Format: 10

Record: (KPSG(L),KPBG(L),KAECG(1))
Partition coefficient of toxicant on compartment sediment. Partition coefficient of toxicant on compartment biomass (BIOMSG). Multiplication of the anion exchange capacity of the system sediments by KAECG gives the partition coefficient on the sediment. Three values per record. Format: 9

Record: (QUANTG(1,L),QUANTG(2,L),QUANTG(3,L))
Same as SPFLG(1)

Record: (ABS4) Absorption spectrum for singly charged anion (SH-). See ABS1. Format: 6

Record: (KDPG(L),RFLATG(L))
Same as SPFLG(1)

Record: (KAHG(1,L),KAHG(2,L),KAHG(3,L))
Same as SPFLG(1)

Record: (EAHG(1,L),EAHG(2,L),EAHG(3,L))
Same as SPFLG(1)

Record: (KNHG(1,L),KNHG(2,L),KNHG(3,L))
Same as SPFLG(1)

Record: (ENHG(1,L),ENHG(2,L),ENHG(3,L))
Same as SPFLG(1)

Record: (KBHG(1,L),KBHG(2,L),KBHG(3,L))
Same as SPFLG(1)

Record: (EBHG(1,L),EBHG(2,L),EBHG(3,L))
Same as SPFLG(1)

Record: (KOXG(1,L),KOXG(2,L),KOXG(3,L))
Same as SPFLG(1)

Record: (EOXG(1,L),EOXG(2,L),EOXG(3,L))
Same as SPFLG(1)

Record: (KBACWG(1,L),KBACWG(2,L),KBACWG(3,L))
Same as SPFLG(1)

Record: (QTBAWG(1,L),QTBAWG(2,L),QTBAWG(3,L))
Same as SPFLG(1)

Record: (KBACSG(1,L),KBACSG(2,L),KBACSG(3,L))
Same as SPFLG(1)

Record: (QTBASG(1,L),QTBASG(2,L),QTBASG(3,L))
Same as SPFLG(1)

3.4.4 Creating or Changing the Environmental Data

Locate the ECO2 record in the environmental data. This record acts as a header/delimiter for the associated parameters. The compartment parameter data are located in the following sequential record layout. (The format code list provides detailed format specifications.)

Record:	(SYSTYP)	Ecosystem name, maximum 60 characters. Format: 1
Record:	(KOUNT)	Number of compartments, maximum number of compartments is NPX, which is fixed for a particular installation. Format: 2
Record:	(TYPEE)	The next KOUNT records each contain a one character compartment code, KOUNT the number of compartments. Format: 3
Record:	(LATG)	Ecosystem latitude, columns 1-10, degrees and seconds as whole number and decimal fraction, e.g. 10.15. Format: 4
Record:	(WINDG)	wind velocity per compartment, eight per record. Format: 5
Record:	(VOLG)	Total environmental volume per compartment. Format: 5
Record:	(AREAG)	Area of each ecosystem compartment. Format: 5
Record:	(DEPTHG)	Average depth of each compartment. Format: 5
Record:	(STFLOG)	Stream flow entering ecosystem compartments. Format: 5
Record:	(STSEDG)	Stream-borne sediment load entering ecosystem compartments. Format: 5
Record:	(NPSFLG)	Non-point-source water flow entering ecosystem compartments. Format: 5
Record:	(NPSEDG)	Non-point-source sediment loads entering ecosystem compartments. Format: 5

Record:	(INTFLG)	Interflow (groundwater seepage) entering each ecosystem compartment. Format: 5
Record:	(RAING)	Average rainfall in geographic area of system. Columns 1-10. Format: 4
Record:	(CLOUDG)	Average cloudiness in tenths of full sky cover. Columns 1-10. Format: 4
Record:	(WLAMG)	Temporally averaged spectral irradiance immediately below the water surface. This is a five record layout containing 39 values, ten columns per value, eight values per record. Format: 6
Record:	(DFACG)	Distribution function (optical path) for each compartment. Format: 5
Record:	(EVAPG)	Evaporative water losses from ecosystem compartments. Format: 5
Record:	(SDCHRG)	For water column compartments the suspended sediment concentration; for benthic sediment compartments the bulk density of the bottom sediment. Format: 5
Record:	(PCTWAG)	Percent water in bottom sediments of benthic compartments. Elements corresponding to water column compartments are not used (dummy values). Format: 5
Record:	(NSPEC1)	Number of active advective transport pathways. Format: 2
Record:	(JFRADG)	Source compartment (J) for advective flow. Format: 7
Record:	(ITOADG)	Receiving compartment (I) for advective flow. Format: 7
Record:	(ADVPRG)	Proportion of total advective flow from compartment J that flows to compartment I. Format: 12
Record:	(NSPEC2)	Number of active dispersive transport pathways. Format: 2
Record:	(JTURBG)	Source compartment for dispersive flow. Format: 7
Record:	(ITURBG)	Receiving compartment for dispersive flow.

Format: 7

Record: (XSTURG) Cross-sectional areas for dispersive exchanges. Format: 12

Record: (CHARLG) Characteristic lengths of dispersive exchange pairings. Format: 12

Record: (DSPG) Eddy dispersion coefficients for dispersive exchange pairings. Format: 12

Record: (FROCG) Organic carbon content of compartment sediments. Format: 5

Record: (CECG) Cation exchange capacity of sediments in each compartment. Format: 5

Record: (AECG) Anion exchange capacity of sediments in each compartment. Format: 5

Record: (TCELG) Average temperature of ecosystem compartments. Format: 5

Record: (PHG) Negative value of log of temporal average of [H+] concentration for each compartment. Format: 5

Record: (POHG) Negative value of log of temporally averaged [OH-] concentration for each compartment. Format: 5

Record: (OXRADG) Molar concentration of environmental oxidants in each ecosystem compartment. Format: 5

Record: (BIOMSG) Total actively sorbing biomass in each compartment. Format: 5

Record: (PLRAG) Planktonic fraction of total biomass in each compartment. Format: 5

Record: (BIOTMG) Biotemperature in each compartment. Format: 5

Record: (BACTOG) Bacterial population density in each compartment. Format: 5

Record: (ACBACG) Proportion of bacterial population that actively degrades toxicant. Format: 5

Record: (KO2G) Rearation parameter in each compartment. Format: 5

Record:	(CMPETG)	Single-valued zenith light extinction coefficient for water columns, dummy variable for benthic compartments. Format: 5
Record:	(DOCG)	Dissolved organic carbon concentration in water column compartments, dummy variable in benthic compartments. Format: 5
Record:	(CHLG)	Concentration of chlorophyll and chlorophyll-like pigments in water column compartments, dummy variable in benthic compartments. Format: 5

SECTION 4

PROGRAMMER'S SUPPLEMENT

4.1 System Documentation

4.1.1 System Overview

EXAMS is a collection of FORTRAN routines that supports batch and interactive modes of operation. The batch version uses a driver routine to process the user's inputs and invoke the simulation program. The interactive version replaces the driver routine with routines that allow the user to interactively specify and alter inputs to the simulation program, invoke the simulation code, and review the results. Both implementations of EXAMS use the same simulation code. Figures 4.1 and 4.2 show the block structure of the batch mode and the interactive mode of operation, respectively.

The batch mode requires a single input stream, e.g. a card reader, and a single output stream, e.g. a line printer. The interactive version communicates with the user via a computer terminal. This version requires a mass storage capability for the chemical and environmental libraries, the online assistance file, the variables description file, the tabular output file, the kinetics output file, and the steady-state output file and, optionally, a line printer for selected outputs.

EXAMS was designed and implemented with the aim of providing a portable code. The code was written in American National Standard FORTRAN X3.9-1966 with only one extension, the DEFINE FILE option. This option provides rapid access to information stored in external files; random access files significantly reduce input/output (I/O) time over that required by sequential access files. The DEFINE FILE option is supported by the majority of minicomputer implementions of FORTRAN, and by most recent versions of FORTRAN on mainframes.

The interactive version of EXAMS executes extensive character string manipulations; the 1966 FORTRAN standard does not support this feature. To ensure portability of EXAMS' character string storage and manipulations, the character strings are stored in an unpacked format, that is, one character per INTEGER location.

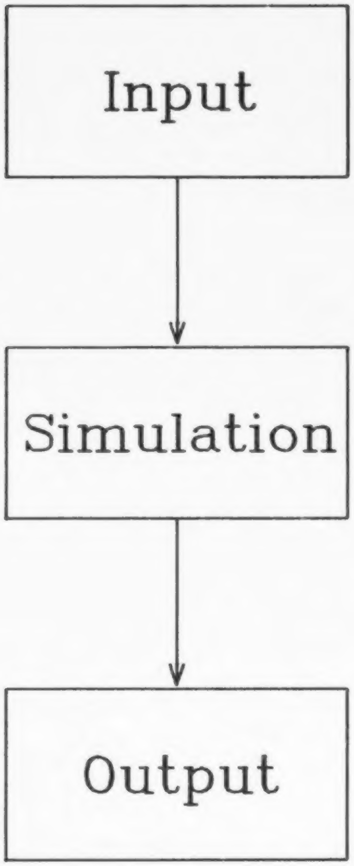
Input
Simulation
Output

Figure 4.1. EXAMS Block Structure for Batch Mode of Operation.

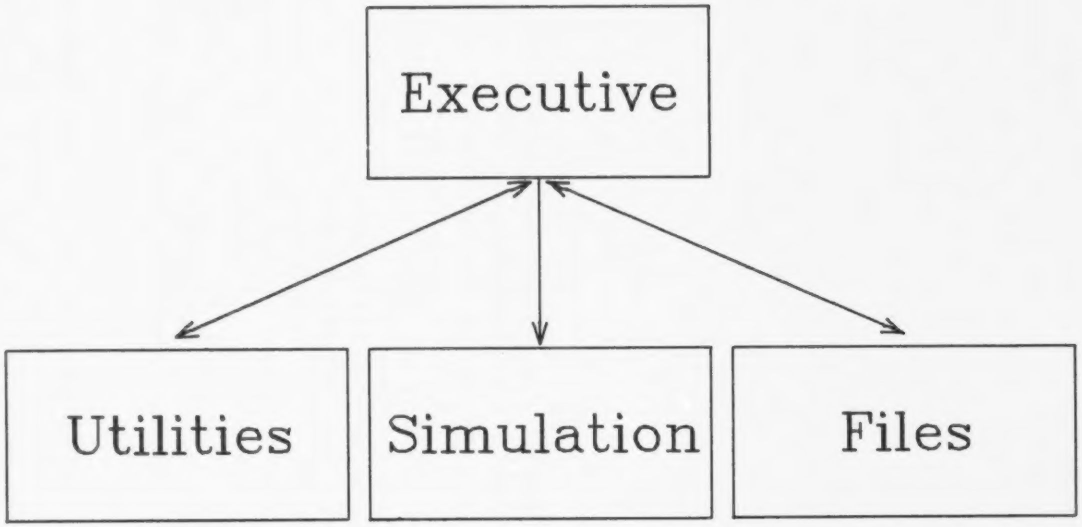
Executive
Utilities
Simulation
Files

Figure 4.2. EXAMS Block Structure for Interactive Mode of Operation.

4.1.2 Resource Requirements

EXAMS has been implemented in FORTRAN IV as defined by the ANS FORTRAN X.39-1966 report. The DEFINE FILE extension of the standard is used for file manipulation, but standard sequential I/O can be substituted with some sacrifice in speed of execution. An overlay capability is required to implement EXAMS on small computers such as the PDP-11 or HP 3000. The batch version requires 64K bytes (overlaid) of memory (for aquatic systems of up to 10 compartments); this version does not require mass storage capabilities. The interactive version also requires 64K bytes (overlaid) of memory, plus an additional mass storage requirement. The interactive version of EXAMS requires 100K bytes of mass storage for utility files, 2K bytes for each chemical in the active files and 2.5K bytes for each active defined environment. Execution times range from a few seconds to several minutes depending on the problem to be solved. The software is distributed on magnetic tape; the source code consists of about 16,000 card images.

4.1.3 System Architecture

The batch version of EXAMS uses a driver routine to process the input stream and invoke the simulation. The input stream defines the simulation to be performed by specifying the name of a compound, the name of an environment, and chemical loadings on the selected environment. The input stream also includes the chemical (compound) database and the environmental database. After the names of the compound and environment and the chemical loadings have been read, the driver sequentially searches the remainder of the input stream (the chemical and environmental databases) for the parameters associated with the compound and environment specified in the input. Because the search is sequential, the order of the data in the input stream is very important, that is, the name of the compound must precede the name of the environment, and the chemical database must precede the environmental database.

When the chemical and environmental data have been extracted from the databases, the driver routine invokes the simulation driver that controls program execution until the simulation is complete. At the conclusion of the simulation, the main driver regains control and execution ends. The main driver routine can be rewritten to execute multiple runs, incorporate plotting and statistical routines, etc. The simulation code need not be modified to support these enhancements.

The elements of a batch input stream occur in the following order (see Section 3.4).

1. Name of compound
2. Name of environment
3. Loadings
4. Chemical database
5. Environmental database

In the interactive version of EXAMS, the main driver routine used with the batch version is replaced with an executive routine, utility routines, and a mass storage database. The executive communicates with the user, deciphers the user's inputs, and takes appropriate action based on these inputs. A user can select compounds and environments, specify chemical loadings, alter parameter values, invoke the simulation program, store and retrieve user-defined chemical and environmental parameters, request online assistance, print inputs and results, and plot the results.

EXAMS acquires input from the user's terminal in the form of a string of characters and deciphers the intent expressed in that string. If the intent is recognized, the action is performed. If it is not recognized, an appropriate message is printed on the terminal. EXAMS' lexical analyzer deciphers the input string by isolating groups of characters into lexical entities called "tokens." The tokens are tested to determine whether they are members of appropriate tables. A table may contain character strings that represent the names of compounds, the names of environments, keywords, etc., depending upon the relative position of the token in the input string. For example, the string

```
CHANGE MWT TO 437
```

has 4 tokens: CHANGE, MWT, TO, and 437. CHANGE is compared with a table of valid EXAMS commands. MWT is compared with a table of names of variables that can be CHANGEd. The token TO makes the expression more readable; it is a necessary portion of the command. The token 437 is converted to a floating point number that is assigned to MWT.

Data elements in the recognition process include: a table of tokens for matching the input string, the total number of tokens, a vector containing the length of each token, and a vector that contains the minimum length of each token required to make it unique. For example, consider:

```
TABLE  = RUNSTOPPLOTCOMPOUNDSHOW
LEN    = 3,4,4,8,4
MIN    = 1,2,1,1,2
NUMBER = 5
```

Five tokens are in the recognition table: "TABLE" "RUN," "STOP," "PLOT," "COMPOUND," and "SHOW"; with corresponding lengths of 3, 4, 4, 8, and 4 characters. The minimum lengths required for uniqueness are 1, 2, 1, 1, and 2, respectively.

The recognition alogrithm first compares the length of the input string with the length of each token in the recognition table. If the length of the input string is greater than the length of the token, the token is ignored. The length of the next token is then tested; this process continues until all entries in the recognition table are exhausted. If the length of the input string is less than or equal to the length of the current token, the token is a possible match. If the minimum length required for uniqueness is less than or equal to the input string, the input string is then compared against the token. If the input string and the token agree, then the input string has been recognized. If they do not agree, then the next token is tested. This procedure continues until a match is made or until all entries in the recognition table have been exhausted. If no match is made, the input string was not recognized.

Consider, for example, an input of "RU." The input string has a computed length of 2. The input length is compared with the length of the first entry in the recognition table (3) and meets the criterion for length. The minimum length for this entry is 1, and this test is also successful. Finally, the character test is performed and a match is established.

4.1.4 Overlay Structure

An overlay structure for the batch version of EXAMS is shown in Figure 4.3 and an overlay structure for the interactive version of EXAMS is shown in Figure 4.4.

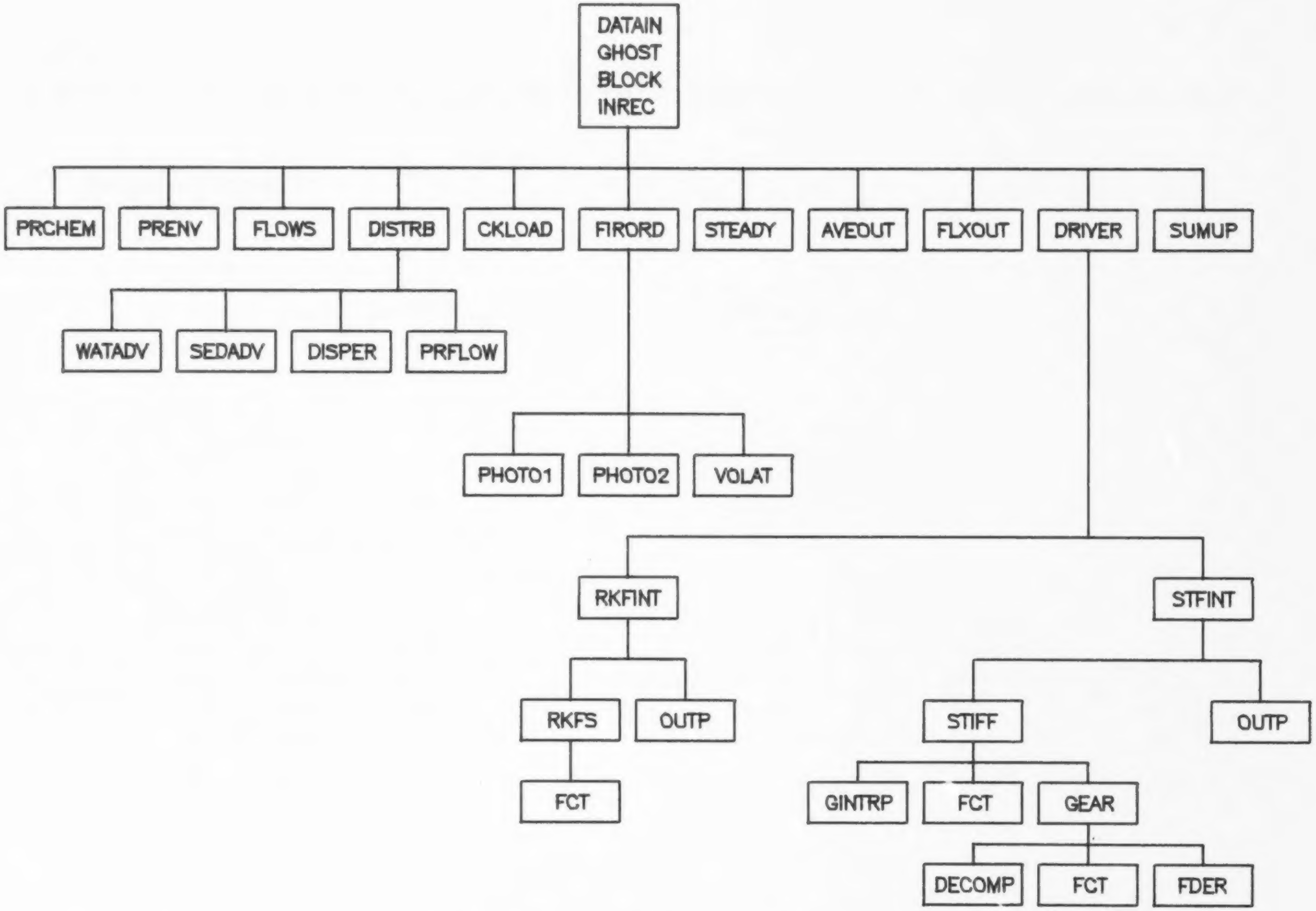
DATAIN
GHOST
BLOCK
INREC
PRCHEM
PRENV
FLOWS
DISTRB
CKLOAD
FIRORD
STEADY
AVEOUT
FLXOUT
DRIVER
SUMUP
WATADV
SEDADV
DISPER
PRFLOW
PHOTO1
PHOTO2
VOLAT
RKFINT
STFINT
RKFS
OUTP
FCT
STIFF
OUTP
GINTRP
FCT
GEAR
DECOMP
FCT
FDER

Figure 4.3. Detailed Block Diagram for the Batch Mode of Operation.

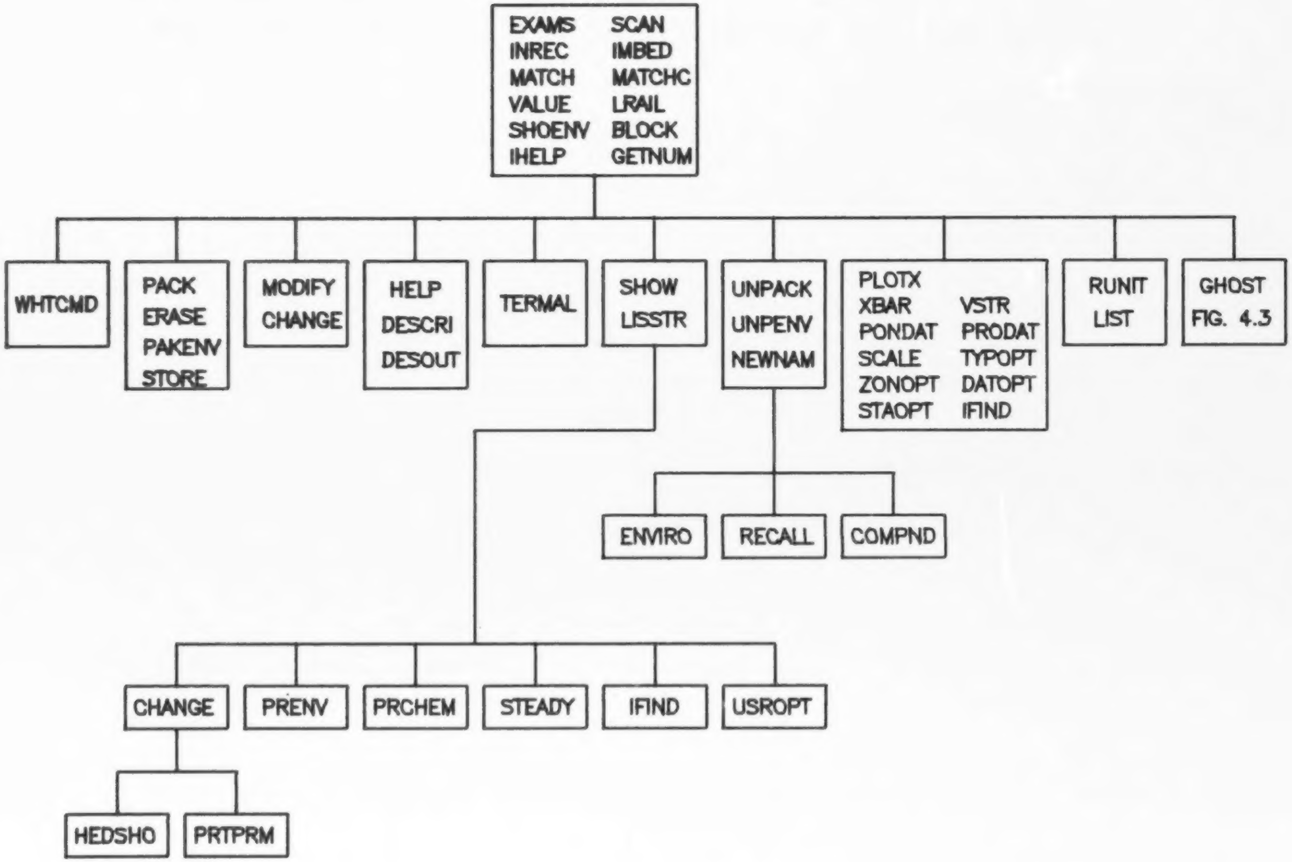
EXAMS SCAN
INREC IMBED
MATCH MATCHC
VALUE LRAIL
SHOENV BLOCK
IHELP GETNUM
WHTCMD
PACK ERASE PAKENV STORE
MODIFY CHANGE
HELP DESCRI DESOUT
TERMAL
SHOW LISSTR
UNPACK UNPENV NEWNAM
PLOTX XBAR PONDAT SCALE ZONOPT STAOPT VSTR PRODAT TYPOPT DATOPT IFIND
RUNIT LIST
GHOST FIG. 4.3
ENVIRO
RECALL
COMPND
CHANGE
PRENV
PRCHEM
STEADY
IFIND
USROPT
HEDSHO
PRTPRM

Figure 4.4. EXAMS Detailed Block Structure for the Interactive Mode of Operation.

4.1.5 File Organization

4.1.5.1 Environmental file

Environmental data are held in a single random access file. The data are segregated into two kinds of environmental definitions: fixed or unCHANGEable data, and a user-defined database available for interactive modification. Both datasets in the file have the same structure, but they are created, stored, and retrieved via different mechanisms.

The "fixed" environmental definitions are included with the EXAMS distribution package. Their names are specified in the BLOCK DATA portion of the code, in the variable "ECONAM." The number of fixed definitions is stored in NOECOS, the vector ECOLEN holds the lengths of the names, and the vector MINECO holds the minimum length required to make each name unique.

The fixed environment definitions are created by a utility routine included in the EXAMS distribution. This utility transfers the definitions from a sequential file to a random access file. These fixed definitions can be retrieved by the user, but these records cannot be altered from an interactive terminal. This restriction was established to forestall inadvertent modifications. The "fixed" database is accessed via a reference to the name of the environment in an "ENVIRONMENT" command.

User-defined environments can be created, stored, retrieved, and erased interactively. A fixed environment definition can be retrieved, altered, and stored in the user-defined portion of the database. "Fixed" databases (especially "UNS," the "unspecified" environment) can be used as templates for loading new environmental definitions (see Section 3.3.4).

User-defined environments are referred to by number, rather than by name. The command "SHOW USER ENVIRONMENTS" displays a table of contents of the user-defined environmental database. All data associated with a user-defined environment can be eliminated via the ERASE command. The command "ERASE ENVIRONMENT N," where N is the number of the environment to be erased, sets all numeric data to zero and all alphabetic data to blanks in the Nth sector of the database.

The size of records in the database is a function of the maximum number of compartments available to a particular installation of EXAMS. This size is defined when EXAMS is compiled. When the size is changed, the data base must be rebuilt. This database is built by a stand-alone utility routine that is included with EXAMS. The data are arranged in the record with the floating point (REAL) quantities first, followed by the integer (INTEGER) quantities. The parameters NPX and NCON are used to define the system size of EXAMS and the layout and size of the records in this file. The location assignments are shown in Table 4.1. The position parameters used in this table (N, M, K, and L) are related to NPX and NCON by: N=4*NCON, M=N+29*NPX, K=L*N, and L=M+42.

4.1.5.2 Chemical file

Chemical data are held in a single random access file. The data are segregated into two kinds of chemical definitions: fixed or unCHANGEable data, and a user-defined database available for interactive modification. Both datasets in the file have the same structure, but they are created, stored, and retrieved via different mechanisms.

The "fixed" chemical definitions are included with the EXAMS distribution package. Their names are specified in the BLOCK DATA portion of the code, in the variable "CMPNAM." The number of fixed definitions is stored in NONAME, the vector NAMLEN holds the lengths of the names, and the vector MINCMP holds the minimum length required to make each name unique.

The fixed chemical definitions are created by a utility routine included in the EXAMS distribution. This routine transfers the definitions from a sequential file to a random access file. These fixed definitions can be retrieved by the user, but these records cannot be altered from an interactive terminal. This restriction was established to forestall inadvertent modifications. The "fixed" database is accessed via a reference to the name of the chemical in a "COMPOUND" command.

User-defined chemicals can be created, stored, retrieved, and erased interactively. A fixed chemical definition can be retrieved, altered, and stored in the user-defined portion of the database. "Fixed" databases (especially "UNS," the "unspecified" chemical) can be used as templates for loading new chemical definitions (see Section 3.3.4).

User-defined chemicals are referred to by number, rather than by name. The command "SHOW USER COMPOUNDS" displays a table of contents of the user-defined chemical database. All data associated with a user-defined chemical can be eliminated via the ERASE command. The command "ERASE COMPOUND N," where N is the number of the chemical to be erased, sets all numeric data to zero and all alphabetic data to blanks in the Nth sector of the database.

This database is built by a stand-alone utility routine that is included with EXAMS. The data are arranged in the record with the floating point (REAL) quantities first, followed by the integer (INTEGER) quantities. The location assignments are shown in Table 4.2.

Table 4.1. Location assignments for environmental file

Starting Position	Ending Position	Length	Name	Type
1	NCON	NCON	XSTURG	REAL
NCON+1	2*NCON	NCON	CHARLG	REAL
2*NCON+1	3*NCON	NCON	DSPG	REAL
3*NCON+1	4*NCON	NCON	ADVPRG	REAL
N+1	N+NPX	NPX	SDCHRG	REAL
N+NPX+1	N+2*NPX	NPX	FROCG	REAL
N+2*NPX+1	N+3*NPX	NPX	CECG	REAL
N+3*NPX+1	N+4*NPX	NPX	AECG	REAL
N+4*NPX+1	N+5*NPX	NPX	PCTWAG	REAL
N+5*NPX+1	N+6*NPX	NPX	TCELG	REAL
N+6*NPX+1	N+7*NPX	NPX	PHG	REAL
N+7*NPX+1	N+8*NPX	NPX	POHG	REAL
N+8*NPX+1	N+9*NPX	NPX	OXRADG	REAL
N+9*NPX+1	N+10*NPX	NPX	BIOMSG	REAL
N+10*NPX+1	N+11*NPX	NPX	PLRAG	REAL
N+11*NPX+1	N+12*NPX	NPX	BIOTMG	REAL
N+12*NPX+1	N+13*NPX	NPX	BACTOG	REAL
N+13*NPX+1	N+14*NPX	NPX	ACBACG	REAL
N+14*NPX+1	N+15*NPX	NPX	KO2G	REAL
N+15*NPX+1	N+16*NPX	NPX	CMPETG	REAL
N+16*NPX+1	N+17*NPX	NPX	VOLG	REAL
N+17*NPX+1	N+18*NPX	NPX	AREAG	REAL
N+18*NPX+1	N+19*NPX	NPX	DEPTHG	REAL
N+19*NPX+1	N+20*NPX	NPX	EVAPG	REAL
N+20*NPX+1	N+21*NPX	NPX	WINDG	REAL
N+21*NPX+1	N+22*NPX	NPX	STFLOG	REAL
N+22*NPX+1	N+23*NPX	NPX	STSEDG	REAL
N+23*NPX+1	N+24*NPX	NPX	NPSFLG	REAL
N+24*NPX+1	N+25*NPX	NPX	NPSEDG	REAL
N+25*NPX+1	N+26*NPX	NPX	INTFLG	REAL
N+26*NPX+1	N+27*NPX	NPX	DFACG	REAL
N+27*NPX+1	N+28*NPX	NPX	DOCG	REAL
N+28*NPX+1	N+29*NPX	NPX	CHLG	REAL
M+1	M+39	39	WLAMG	REAL
M+40	M+40	1	CLOUDG	REAL
M+41	M+41	1	RAING	REAL
M+42	M+42	1	LATG	REAL
L+1	L+NCON	NCON	JFRADG	INTEGER
L+NCON+1	L+2*NCON	NCON	ITOADG	INTEGER
L+2*NCON+1	L+3*NCON	NCON	JTURBG	INTEGER
L+3*NCON+1	L+4*NCON	NCON	ITURBG	INTEGER
K+1	K+1	1	KOUNT	INTEGER
K+2	K+NPX+1	NPX	TYPEE	INTEGER
K+NPX+2	K+NPX+61	60	SYSTYP	INTEGER

Table 4.2. Location assignments for chemical file

Starting Position	Ending Position	Length	Name	Type
1	1	1	MWTG	REAL
2	6	5	SOLG	REAL
7	11	5	ESOLG	REAL
12	13	2	PKBG	REAL
14	15	2	EPKBG	REAL
16	17	2	PKAG	REAL
18	19	2	EPKAG	REAL
20	24	5	KPSG	REAL
25	29	5	KPBG	REAL
30	30	1	KOCG	REAL
31	31	1	KOWG	REAL
32	33	2	KCECG	REAL
34	35	1	KAECG	REAL
36	36	1	KVOG	REAL
37	37	1	HENRYG	REAL
38	38	1	VAPRG	REAL
39	39	1	EVPRG	REAL
40	54	1	QUANTG	REAL
55	59	5	KDPG	REAL
60	74	15	KAHG	REAL
75	89	15	EAHG	REAL
90	104	15	KNHG	REAL
105	119	15	ENHG	REAL
120	134	15	KBHG	REAL
135	149	15	EBHG	REAL
150	164	15	KOXG	REAL
165	179	15	EOXG	REAL
180	194	15	KBACWG	REAL
195	209	15	QTBAWG	REAL
210	224	15	KBACSG	REAL
225	239	15	QTBASG	REAL
240	244	5	RFLATG	REAL
245	439	195	ABSG	REAL
440	440	1	LAMAXG	REAL
441	441	1	EHENG	REAL
442	446	5	SPFLG	INTEGER
447	506	60	CHEMNA	INTEGER

4.1.5.3 Online assistance file

The online assistance database is a sequential file; it is organized by keywords. These keywords are designated by a "$" in the first position of a record. Information for a given keyword continues until the next occurrence of a record with "$" in position 1. The records are 80 characters long and a record with "$END" signals the end of the file.

4.1.5.4 Labeled COMMON variables file

This file is accessed in response to the HELP <variable name> command. The names of the variables are specified in the BLOCK DATA portion of the EXAMS code in the variable "MODS." The number of descriptions is stored in NOMOD, the vector MODLEN holds the lengths of the names, and the vector MODMIN holds the minimum length required to make each of the names unique.

The database is organized as a random access file. Each record of the database corresponds to the name of a labeled common variable and is 800 characters long. The database records are created by a utility routine included in the EXAMS distribution. This routine transfers the descriptions from a sequential file to a random access file.

4.1.7 Organization of EXAMS' Labeled COMMONs

EXAMS labeled COMMONS are described in Tables 4.3 through 4.23.

Table 4.3 Labeled COMMON BACTG sorted by name and by position.

Name	Position	Length	Name	Position	Length
KBACSG	31-45	15	KBACWG	1-15	15
KBACWG	1-15	15	QTBAWG	16-30	15
QTBASG	46-60	15	KBACSG	31-45	15
QTBAWG	16-30	15	QTBASG	45-60	15

Table 4.4 Labeled COMMON CLIMG sorted by name and by position.

Name	Position	Length	Name	Position	Length
EVAPG	2-11	10	RAING	1	1
LATG	12	1	EVAPG	2-11	10
RAING	1	1	LATG	12	1
WINDG	13-22	10	WINDG	13-22	10

Table 4.5 Labeled COMMON CONTRG sorted by name and by position.

Name	Position	Length	Name	Position	Length
SPFLG	1	5	SPFLG	1	6

Table 4.6 Labeled COMMON DPHOTG sorted by name and by position.

Name	Position	Length	Name	Position	Length
ABSG	26-220	195	QUANTG	1-15	15
KDPG	16-20	5	KDPG	16-20	5
LAMAXG	221	1	RFLATG	21-25	5
QUANTG	1-15	15	ABSG	26-220	195
RFLATG	21-25	5	LAMAXG	221	1

Table 4.7 Labeled COMMON FLOWG sorted by name and by position.

Name	Position	Length	Name	Position	Length
INTFLG	41-50	10	STFLOG	1-10	10
NPSEDG	31-40	10	STSEDG	11-20	10
NPSFLG	21-30	10	NPSFLG	21-30	10
STFLOG	1-10	10	NPSEDG	31-40	10
STSEDG	11-20	10	INTFLG	41-50	10

Table 4.8 Labeled COMMON GEOMT sorted by name and by position.

Name	Position	Length	Name	Position	Length
AREAG	11-20	10	VOLG	1-10	10
DEPTHG	21-30	10	AREAG	11-20	10
VOLG	1-10	10	DEPTHG	21-30	10

Table 4.9 Labeled COMMON HYDROG sorted by name and by position.

Name	Position	Length	Name	Position	Length
EAHG	16-30	15	KAHG	1-15	15
EBHG	76-90	15	EAHG	16-30	15
ENHG	46-60	15	KNHG	31-45	15
KAHG	1-15	15	ENHG	46-60	15
KBHG	61-75	15	KBHG	61-75	15
KNHG	31-45	15	EBHG	76-90	15

Table 4.10 Labeled COMMON INPAR sorted by name and by position.

Name	Position	Length	Name	Position	Length
AUDIT	110	1	NOCREC	1	1
CMDLEN	7-26	20	NOEREC	2	1
CMPNAM	1236-1445	210	START	3	1
COMVAR	594-613	20	STOP	4	1
ECOLEN	89-108	20	TYPE	5	1
ECONAM	1446-1545	100	NCMDS	6	1
HELEN	855-904	50	CMDLEN	7-26	20
HELPS	2046-2345	300	NONAME	27	1
IENV	955	1	NAMLEN	28-87	60
INPUT	1056-1135	80	NOECOS	88	1
MINCMD	976-995	20	ECOLEN	89-108	20
MINCMP	996-1055	60	POUND	109	1
MINECO	956-975	20	AUDIT	110	1
MINHLP	905-954	50	NOMOD	111	1
MODLEN	112-231	120	MODLEN	112-231	120
MODMIN	233-352	120	TERMTY	232	1
MODS	1546-2045	500	MODMIN	233-352	120
NAMLEN	28-87	60	TS	353-472	120
NCMDS	6	1	TD	473-592	120
NOCOM	593	1	NOCOM	593	1
NOCREC	1	1	COMVAR	594-613	20
NOECOS	88	1	TROW	614-733	120
NOEREC	2	1	TCOL	734-853	120
NOHELP	854	1	NOHELP	854	1
NOMOD	111	1	HELEN	855-904	50
NONAME	27	1	MINHLP	905-954	1
POUND	109	1	IENV	955	1
PRICMD	1136-1235	100	MINECO	956-975	20
START	3	1	MINCMD	976-995	20
STOP	4	1	MINCMP	996-1055	60
TCOL	734-853	120	INPUT	1056-1135	80
TD	473-592	120	PRICMD	1136-1235	100
TERMTY	232	1	CMPNAM	1236-1445	210
TROW	614-733	120	ECONAM	1446-1545	100
TS	353-472	120	MODS	1546-2045	500
TYPE	5	1	HELPS	2046-2345	300

Table 4.11 Labeled COMMON IONG sorted by name and by position.

Name	Position	Length	Name	Position	Length
EPKAG	7-8	2	PKBG	1-2	2
EPKBG	3-4	2	EPKBG	3-4	2
PKAG	5-6	2	PKAG	5-6	2
PKBG	1-2	2	EPKAG	7-8	2

Table 4.12 Labeled COMMON LOADSG sorted by name and by position.

Name	Position	Length	Name	Position	Length
DRFLDG	31-40	10	STRLDG	1-10	10
IFLLDG	41-50	10	NPSLDG	11-20	10
NPSLDG	11-20	10	PCPLDG	21-30	10
PCPLDG	21-30	10	DRFLDG	31-40	10
STRLDG	1-10	10	IFLLDG	41-50	10

Table 4.13 Labeled COMMON NAME1G sorted by name and by position.

Name	Position	Length	Name	Position	Length
CHEMNA	1	60	CHEMNA	1	60

Table 4.14 Labeled COMMON NAME2G sorted by name and by position.

Name	Position	Length	Name	Position	Length
SYSTYP	1-60	60	SYSTYP	1-60	60
TYPEE	61-70	10	TYPEE	61-70	10

Table 4.15 Labeled COMMON OXIDG sorted by name and by position.

Name	Position	Length	Name	Position	Length
EOXG	16-30	15	KOXG	1-15	15
KOXG	1-15	15	EOXG	16-30	15

Table 4.16 Labeled COMMON PARTG sorted by name and by position.

Name	Position	Length	Name	Position	Length
KAECG	15-16	2	KPSG	1-5	5
KCECG	13-14	2	KPBG	6-10	5
KOCG	11	1	KOCG	11	1
KOWG	12	1	KOWG	12	1
KPBG	6-10	5	KCECG	13-14	2
KPSG	1-5	5	KAECG	15-16	2

Table 4.17 Labeled COMMON PCHEMG sorted by name and by position.

Name	Position	Length	Name	Position	Length
ESOLG	7-11	5	MWTG	1	1
MWTG	1	1	SOLG	2-6	5
SOLG	2-6	5	ESOLG	7-11	5

Table 4.18 Labeled COMMON PHOG sorted by name and by position.

Name	Position	Length	Name	Position	Length
CHLG	21-30	10	CMPETG	1-10	10
CLOUDG	70	1	DOCG	11-20	10
CMPETG	1-10	10	CHLG	21-30	10
DGACG	71-80	10	WLAMG	31-69	39
DOCG	11-20	10	CLOUDG	70	1
WLAMG	31-69	39	DFACG	71-80	10

Table 4.19 Labeled COMMON QUALG sorted by name and by position.

Name	Position	Length	Name	Position	Length
ACBACG	81-90	10	TCELG	1-10	10
BACTOG	71-80	10	PHG	11-20	10
BIOMSG	41-50	10	POHG	21-30	10
BIOTMG	61-70	10	OXRADG	31-40	10
KO2G	91-100	10	BIOMSG	41-50	10
OXRADG	31-40	10	PLRAG	51-60	10
PHG	11-20	10	BIOTMG	61-70	10
PLRAG	51-60	10	BACTOG	71-80	10
POHG	21-30	10	ACBACG	81-90	10
TCELG	1-10	10	KO2G	91-100	10

Table 4.20 Labeled COMMON SEDG sorted by name and by position.

Name	Position	Length	Name	Position	Length
AECG	31-40	10	SDCHRG	1-10	10
CECG	21-30	10	FROCG	11-20	10
FROCG	11-20	10	CECG	21-30	10
PCTWAG	41-50	10	AECG	31-40	10
SDCHRG	1-10	10	PCTWAG	41-50	10

Table 4.21 Labeled COMMON SETUPG sorted by name and by position.

Name	Position	Length	Name	Position	Length
ADVPRG	62-91	30	KOUNT	1	1
BATCH	242	1	JFRADG	2-31	30
CHARLG	182-211	30	ITOADG	32-61	30
DSPG	212-241	30	ADVPRG	62-91	30
ITOADG	32-61	30	JTURBG	92-121	30
ITURBG	122-151	30	ITURBG	122-151	30
JFRADG	2-31	30	XSTURG	152-181	30
JTURBG	92-121	30	CHARLG	182-211	30
KOUNT	1	1	DSPG	212-241	30
XSTURG	152-181	30	BATCH	242	1

Table 4.22 Labeled COMMON UNITS sorted by name and by position.

Name	Position	Length	Name	Position	Length
AUDOUT	6	1	RPTOUT	1	1
INCOMP	7	1	SSOUT	2	1
INDEF	8	1	KINOUT	3	1
INENVR	10	1	TTYIN	4	1
INHLP	9	1	TTYOUT	5	1
KINOUT	3	1	AUDOUT	6	1
RPTOUT	1	1	INCOMP	7	1
SSOUT	2	1	INDEF	8	1
TTYIN	4	1	INHLP	9	1
TTYOUT	5	1	INENVR	10	1

Table 4.23 Labeled COMMON VOLATG sorted by name and by position.

Name	Position	Length	Name	Position	Length
EHENG	3	1	KVOG	1	1
EVPRG	5	1	HENRYG	2	1
HENRYG	2	1	EHENG	3	1
KVOG	1	1	VAPRG	4	1
VAPRG	4	1	EVPRG	5	1

4.2 Implementation Notes

4.2.1 PDP-11/70, IAS, Batch Version

1. Mount the Files-11 tape, e.g.,

```
MOUNT/NOOP/DEN:1600 MM0: EXAMS
```

2. COPY MM0:*.*;* *.*;*

3. Execute the command files FOTOX.CMD and LNTOX.CMD to compile and task-build EXAMS.

4. Run EXAMS as follows.

```
PDS> RUN EXAMS
```

The results should be compared with the sample output listing supplied with the distribution package (Section 3.1) to verify that EXAMS has been installed correctly.

4.2.2 PDP-11/70, IAS, Interactive Version

1. Mount the Files-11 tape, e. g.,

```
MOUNT/NOOP/DEN:1600 MM0: EXAMS
```

2. COPY MM0:[*,*]*.*;* *.*;*

3. Edit file BUILD.BIS TO REFLECT YOUR USER IDENTIFICATION ON THE "$JOB" CARD.

4. SUBMIT FILE BUILD.BIS to the batch stream. BUILD.BIS creates the necessary random access files used by EXAMS and the EXAMS task image. When the batch job finishes EXAMS is ready for use and may be invoked by entering the following command.

```
PDS> RUN EXAMS
```

4.2.3 IBM-370, OS/MVS, Batch Version

1. Because of the wide variety of IBM 360/370/3032/3033 configurations, a specific instruction for the installation of EXAMS is not provided. The JCL that was used to install EXAMS on EPA's IBM computer is provided as a guide, however.

```
Installation dependent JOB card
//S EXEC FORTHCLG
//FORT.SYSIN DD *

                File No. 6 of the distribution tape.

//LKED.SYSLMOD DD DISP=(NEW,CATLG)
//   VOL=SER=USERXX,
//  UNIT=3330-1,SPACE=(TRK,20,20,1),RLSE),
//   DCB=BLKSIZE=13030,
//   DSN=AESOP(AESOP)
//GO.FT03F001 DD DUMMY,DCB=BLKSIZE=1000
//GO.FT04F001 DD DUMMY,DCB=BLKSIZE=1000
//GO.SYSIN DD *

File No. 7 of the distribution tape

File No. 8 of the distribution tape

File No. 9 of the distribution tape
```

Note: Either the 'G' or the 'H' level FORTRAN compiler can be used. The results should be compared with the enclosed sample output listing (Section 3.1) to verify that EXAMS has been installed correctly.

2. The following JCL is used to execute EXAMS from the stored load module.

```
Installation dependent JOB card
//GO EXEC PGM=AESOP
//STEPLIB DD DISP=SHR,DSN=AESOP
//GO.FT03F001 DD DUMMY,DCB=BLKSIZE=1000
//GO.FT04F001 DD DUMMY,DCB=BLKSIZE=1000
//GO.FT06F001 DD SYSOUT=A,DCB=(LRECL=133,RECFM=FBA,BLKSIZE=1330)
//GO.FT05F001 DD *

FILE NO. 7 OF THE DISTRIBUTION TAPE

FILE NO. 8 OF THE DISTRIBUTION TAPE

FILE NO. 9 OF THE DISTRIBUTION TAPE
```

4.2.4 IBM TSO Interactive 10-Compartment Version

File 1 contains a sample run stream that can be used to build the compound and environment files. The run stream:

1. Creates a skeletal random access file for the chemical data. The file that is created ("COMPOUND.DATA,") is accessed by EXAMS via Logical Unit Number (LUN) 7. In order to accommodate 506 REAL variables, the record length for this file is 2024 bytes.

2. Creates a skeletal random access file for environmental data. The file that is created ("ENVIRO.DATA,") is referred to by EXAMS as LUN 10. In order to accommodate 643 REAL variables, the record length for this file is 2572 bytes.

3. Transfers the information stored in the sequential datasets defined by FORTRAN units 1 and 2 to the random access datasets created in steps 1 and 2.

The run stream should be modified to conform with your installation policies.

File 2 contains a sample run stream used to build the sequential file required to support the on-line HELP utility. The file, HELP.DATA, is 80 characters long and is referred to by EXAMS as LUN 9.

File 3 contains a sample run stream used to build the random access file, DESDEF.DATA, that supports the on-line "HELP variable" and "DESCRIBE variable" commands. The records in the file are 800 characters long; the file is accessed by EXAMS via LUN 8.

File 4 contains the EXAMS source code without any job control language. The code consists of 9619 source images and 6052 comment images. The code should be compiled and linked into a dataset that is accessible by TSO.

File 5 contains a sample TSO CLIST that can be used to allocate the datasets necessary to execute EXAMS.

4.3 Special Installations

4.3.1 EXAMS at NCC-IBM

To use the interactive version of EXAMS at NCC-IBM, the following steps should be issued while logged on to TSO.

> This first step need be executed only once. It copies the necessary datasets to your account; these datasets assume permanent residence on your account.

```
EXEC 'CN.EPADMC.A324.COPY10.CLIST'
```

> Thereafter, execute EXAMS, by entering the following command:

```
EXEC EXAMS10
```

An introductory message will be printed at your terminal, followed by the EXAMS prompt:

```
EXAMS >
```

A listing of dataset, EXAMS10.CLIST, follows.

```
FREEALL
ATTRIB INPUT RECFM(F)  LRECL(80)
ALLOCATE DATASET(*) FILE(FT05F001) USING(INPUT)
ALLOCATE DATASET(*) FILE(FT06F001)
ALLOCATE DATASET(COMPOUND.DATA) FILE(FT07F001) SHR
ALLOCATE DATASET(ENVIRO.DATA) FILE (FT10F001) SHR
ALLOCATE DATASET(DESDEF.DATA) FILE(FT08F001) SHR
ALLOCATE DATASET(HELP.DATA) FILE(FT09F001) SHR
ATTRIB FT02 RECFM(F) LRECL(80)   BLKSIZE(800)
ATTRIB FT03 RECFM(V S) LRECL(80)   BLKSIZE(800)
ATTRIB FT04 RECFM(V S) LRECL(80)   BLKSIZE(800)
ALLOC DA(TEMP1) F(FT02F001) NEW DELETE USING(FT02)-
BLOCK(800) SPACE(50,50)
ALLOC DA(TEMP2) F(FT03F001) NEW DELETE USING(FT03)-
BLOCK(800) SPACE(50,50)
ALLOC DA(TEMP3) F(FT04F001) NEW DELETE USING(FT04)-
BLOCK(800) SPACE(50,50)
CALL EXAMS10(EXAMS10)
```

The load module for the batch version of EXAMS is cataloged and named:

```
CN.EPADMC.A324.EXAMS10B.LOAD(EXAMS10B)
```

REFERENCES

Alexander, M. 1979a. Recalcitrant molecules, fallible micro-organisms. pp. 246-253 In: J.M. Lynch and N.J. Poole (Eds.). Microbial Ecology: A Conceptual Approach. Blackwell Scientific Publications, Oxford.

Alexander, M. 1979b. Biodegradation of toxic chemicals in water and soil. pp. 179-190 In: R. Haque (Ed.) Dynamics, Exposure, and Hazard Assessment of Toxic Chemicals. Ann Arbor Science Publishers, Ann Arbor, Michigan.

Alexander, M. 1981. Biodegradation of chemicals of environmental concern. Science 211:132-138.

APHA 1976. Standard Methods for the Examination of Water and wastewater (Fourteenth Edition). American Public Health Association, Washington, D.C. 1193 pp.

Bailey, G.W., and S.W. Karickhoff. 1973. An ultraviolet spectroscopic method for monitoring surface acidity of clay minerals under varying water content. Clays and Clay Minerals 21:471-477.

Bailey, R.A., H.M. Clarke, J.P. Ferris, S. Krause, and R.L. Strong. 1978. Chemistry of the Environment. Academic Press, New York. 575 pp.

Baird, R.B., C.L. Kuo, J.S. Shapiro, and W.A. Yanko. 1974. The fate of phenolics in wastewater -- determination by direct-injection GLC and Warburg respirometry. Arch. Environ. Contam. Toxicol. 2:165-178.

Balzani, V., and V. Carassiti. 1970. Photochemistry of Coordination Compounds. Academic Press, London and New York. 432 pp.

Banerjee, S., S.H. Yalkowsky, and S.C. Valvani. 1980. Water solubility and octanol/water partition coefficients of organics. Limitations of the solubility-partition coefficient correlation. Environ. Sci. Technol. 14:1227-1229.

Banks, R.B. 1975. Some features of wind action on shallow lakes. J. Environ. Eng. Div., Proc. ASCE 101(EE5):813-827.

Banks, R.B., and F.F. Herrera. 1977. Effect of wind and rain on surface reaeration. J. Environ. Eng. Div., Proc. ASCE 103(EE3): 489-504.

Baughman, G.L., and L.A. Burns. 1980. Transport and transformation of chemicals: A perspective. pp. 1-17 In: O. Hutzinger (Ed.) The Handbook of Environmental Chemistry, Volume 2 Part A -- Reactions and Processes. Springer-Verlag, Berlin-Heidelberg-New York.

Baughman, G.L., D.F. Paris, and W.C. Steen. 1980. Quantitative expression of biotransformation rate. pp. 105-111 In: A.W. Maki, K.L. Dickson, and J.C. Cairns, Jr. (Eds.) Biotransformation and Fate of Chemicals in the Aquatic Environment. American Society for Microbiology, Washington, D.C.

Behrens, J.C. 1979. An exemplified semi-analytical approach to the transient sensitivity of non-linear systems. Appl. Math. Modelling 3:105-115.

Bender, M.L., and M.S. Silver. 1963. The hydrolysis of substituted 2-phenyl-1,3-dioxanes. J. Amer. Chem. Soc. 85:3006-3010.

Berner, R.A. 1976. The benthic boundary layer from the viewpoint of a geochemist. pp. 33-55 In: I.N. McCave (Ed.) The Benthic Boundary Layer. Plenum Press, New York and London.

Berner, R.A. 1980. Early Diagenesis: A Theoretical Approach. Princeton University Press, Princeton, N.J. 241 pp.

Bird, R.B., W.E. Stewart, and E.N. Lightfoot. 1960. Transport Phenomena. John Wiley and Sons, Inc. New York. 780 pp.

Brooks, G.T. 1972. Pesticides in Britain. pp. 61-114 In: F. Matsumura, G.M. Boush, and T. Misato. (Eds.) Environmental Toxicology of Pesticides. Academic Press, New York and London.

Brunskill, G.J., and D.W. Schindler. 1971. Geography and bathymetry of selected lake basins, Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Bd. Canada 28:139-155.

Bunnett, J.F. 1961. The interpretation of rate data. pp. 177-283 In: S.L. Friess, E.S. Lewis, and A. Weissberger (Eds.). Technique of Organic Chemistry Vol. VIII Part I. Interscience Publ. Inc., New York.

Buttner, K. 1938. Physik. Bioklimat. Leipzig. (cited from Zepp 1980)

Buzzell, J.C., Jr., C.H. Thompson, and D.W. Ryckman. 1969. Behavior of Organic Chemicals in the Aquatic Environment. Part III -- Behavior in Aerobic Treatment Systems (Activated Sludge). Manufacturing Chemists Association, Washington, D.C. 84 pp.

Callahan, M.A., M.W. Slimak, N.W. Gabel, I.P. May, C.F. Fowler, J.R. Freed, P. Jennings, R.L. Durfee, F.C. Whitmore, B. Maestri, W.R. Mabey, B.R. Holt, and C. Gould. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. Vol. II: Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, and Miscellaneous Compounds. U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029b. 714 pp.

Calvert, J.G., and J.N. Pitts, Jr. 1966. Photochemistry. John Wiley and Sons, Inc., New York. 899 pp.

Castellan, G.W. 1964. Physical Chemistry. Addison-Wesley Publ. Co., Reading, Massachusetts. 717 pp.

Chiou, C.T., L.J. Peters, and V.H. Freed. 1979. A physical concept of soil-water equilibria for nonionic organic coupounds. Science 206:831-832.

Cohen, Y., W. Cocchio, and D. Mackay. 1978. Laboratory study of liquid-phase controlled volatilization rates in presence of wind waves. Environ. Sci. Technol. 12:553-558.

Copeland, B.J., and W.R. Duffer. 1964. Use of a clear plastic dome to measure gaseous diffusion rates in natural waters. Limnol. Oceanogr. 9:494-499.

Danckwerts, P.V. 1970. Gas-Liquid Reactions. McGraw-Hill Book Co., New York. 276 pp.

Darkis, F.R., H.E. Vermillion, and P.M. Gross. 1940. p-Dichlorobenzene as a vapor fumigant. Physical and chemical studies. Ind. Eng. Chem. 32: 946-949.

Dilling, W.L. 1977. Interphase transfer processes. II. Evaporation rates of chloro methanes, ethanes, ethylenes, propanes, and propylenes from dilute aqueous solutions. Comparisons with theoretical predictions. Environ. Sci. Technol. 11:405-409.

Dilling, W.L., N.B. Tefertiller, and G.J. Kallos. 1975. Evaporation rates and reactivities of methylene chloride, chloroform, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and other chlorinated compounds in dilute aqueous solutions. Environ. Sci. Technol. 9:833-838.

Dobbins, W.E. 1964. Mechanism of gas absorption by turbulent liquids. pp. 61-76 In: W.W. Eckenfelder (Ed.) Advances in Water Pollution Research. Proceedings of the International Conference held in London September 1962. Vol. 2. The MacMillan Company, New York.

Dozier, J. 1980. A clear-sky spectral solar radiation model for snow-covered mountainous terrain. Water Resour. Res. 16:709-718.

Emerson, S. 1975. Gas exchange rates in small Canadian Shield lakes. Limnol. Oceanogr. 20:754-761.

Fischer, H.B., E.J. List, R.C.Y. Koh, J. Imberger, and N.H. Brooks. 1979. Mixing in Inland and Coastal Waters. Academic Press, New York. 483 pp.

Fletcher, M. 1979. The aquatic environment. pp. 92-114 In: J.M. Lynch and N.J. Poole (Eds.) Microbial Ecology: A Conceptual Approach. Blackwell Scientific Publications, Oxford.

Gibbs, R.J. (Ed.) 1977. Transport Processes in Lakes and Oceans. Plenum Press, New York and London. 288 pp.

Green, A.E.S., K.R. Cross, and L.A. Smith. 1980. Improved analytic characterization of ultraviolet skylight. Photochem. Photbiol. 31: 59-65.

Green, A.E.S., T. Sawada, and E.P. Shettle. 1974. The middle ultraviolet reaching the ground. Photochem. Photobiol. 19:251-259.

Green, A.E.S., and P.F. Schippnick. 1980. UV-B reaching the ground. Preliminary manuscript for Conference in Ultraviolet Light in Marine Ecosystems, Copenhagen July 28-31 1980. (unpublished report)

Guinasso, N.L., Jr., and D.R. Schink. 1975. Quantitative estimates of biological mixing rates in abyssal sediments. J. Geophys. Res. 80: 3032-3043.

Hall, C.A.S. 1970. Migration and Metabolism in a Stream Ecosystem. Ph.D. Thesis. University of North Carolina at Chapel Hill.

Haque, R. (Ed.) 1980. Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. Ann Arbor Science Publ. Inc., Ann Arbor, Michigan. 496 pp.

Heathershaw, A.D. 1974. "Bursting" phenomena in the sea. Nature 248: 394-395.

Heathershaw, A.D. 1976. Measurements of turbulence in the Irish Sea benthic boundary layer. pp. 11-31 In: I.N. McCave (Ed.) The Benthic Boundary Layer. Plenum Press, New York and London.

Hill, J., IV., H.P. Kollig, D.F. Paris, N.L. Wolfe, and R.G. Zepp. 1976. Dynamic Behavior of Vinyl Chloride in Aquatic Ecosystems. U.S. Environmental Protection Agency, Athens, Georgia. EPA-600/3-76-001. 64 pp.

Hojerslev, N.K. 1973. Inherent and apparent optical properties of the western Mediterranean and the Hardangerfjord. Univ. Copenhagen, Inst. Phys. Oceanogr. Rep., 21: 70 pp. (cited from Jerlov 1976)

Hojerslev, N.K. 1974. Inherent and apparent optical properties of the Baltic. Univ. Copenhagen, Inst. Phys. Oceanogr. Rep., 23: 70 pp. (cited from Jerlov 1976)

Holley, E.R. 1977. Oxygen transfer at the air-water interface. pp. 117-150 In: R.J. Gibbs (Ed.) Transport Processes in Lakes and Oceans. Plenum Press, New York and London.

Hutchinson, G.E. 1957. A Treatise on Limnology. Vol. I. Geography, Physics, and Chemistry. John Wiley and Sons, Inc., New York. 1015 pp.

Hutzinger, O. (Ed.) 1980. The Handbook of Environmental Chemistry. Volume 2 Part A -- Reactions and Processes. Springer-Verlag, Berlin- Heidelberg-New York. 307 pp.

Hutzinger, O., I.H. van Lelyveld, and B.C.J. Zoeteman. (Eds.) 1978. Aquatic Pollutants: Transformation and Biological Effects. Pergamon Press, Oxford. 519 pp.

Imboden, D.M., and A. Lerman. 1978. Chemical models of lakes. pp. 341-356 In: A. Lerman (Ed.) Lakes -- Chemistry, Geology, Physics. Springer- Verlag, New York.

Israelsen, O.W., and V.E. Hansen. 1962. Irrigation Principles and Practices. John Wiley and Sons, Inc., New York. 447 pp.

Jacobson, S.N., N.L. O'Mara, and M. Alexander. 1980. Evidence for cometabolism in sewage. Appl. Environ. Microbiol. 40:917-921.

Jannasch, H.W., and G.E. Jones. 1959. Bacterial populations in sea water as determined by different methods of enumeration. Limnol. Oceanog. 4:128-139.

Jerlov, N.G. 1976. Marine Optics. Elsevier Oceanography Series, 14. Elsevier Sci. Publ. Co., Amsterdam-Oxford-New York. 231 pp.

Jerlov(Johnson), N.G., and G. Liljeguist. 1938. On the angular distribution of submarine daylight and the total submarine illumination. Sven. Hydrogr.-Biol. Komm. Skr., Ny Ser. Hydrogr. 14: 15 pp. (cited from Jerlov 1976)

Jones, B.F., and C.J. Bowser. 1978. The mineralogy and related chemistry of lake sediments. pp. 179-235 In: A. Lerman (Ed.) Lakes -- Chemistry, Geology, and Physics. Springer-Verlag, New York.

Karickhoff, S.W., and G.W. Bailey. 1976. Protonation of organic bases in clay-water systems. Clays and Clay Minerals 24:170-176.

Karickhoff, S.W., and D.S. Brown. 1978. Paraquat sorption as a function of particle size in natural sediments. J. Environ. Qual. 7:246-252.

Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13:241-248.

Kirby, A.J. 1972. Hydrolysis and formation of esters of organic acids. pp. 57-207 In: C.H. Bamford and C.F.H. Tipper (Eds.) Comprehensive Chemical Kinetics Vol. 10 -- Ester Formation and Hydrolysis and Related Reactions. Elsevier Publishing Co., Amsterdam-London-New York.

Kramer, G.R. 1974. Predicting reaeration coefficients for polluted estuary. J. Envir. Eng. Div., Proc. ASCE 100(EE1):77-92.

Lassiter, R.R., G.L. Baughman, and L.A. Burns. 1979. Fate of toxic organic substances in the aquatic environment. pp. 219-246 In: S.E. Jorgensen (Ed.) State-of-the-Art in Ecological Modelling. Proceedings of the Conference on Ecological Modelling, Copenhagen, Denmark 28 August - 2 September 1978. International Society for Ecological Modelling, Copenhagen.

Leighton, P.A. 1961. Solar radiation and its absorption. pp. 6-41 In: P.A. Leighton. Photochemistry of Air Pollution. Academic Press, New York and London.

Leo, A., C. Hansch, and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev. 71:525-616.

Lerman, A. (Ed.) 1978. Lakes -- Chemistry, Geology, Physics. Springer-Verlag, New York. 363 pp.

Li, Y.-H. 1973. Vertical eddy diffusion coefficient in Lake Zurich. Schweiz. Z. Hydrol. 35:1-7.

Liss, P.S. 1973. Processes of gas exchange across an air-water interface. Deep-Sea Res. 20:221-238.

Liss, P.S., and P.G. Slater. 1974. Flux of gases across the air-sea interface. Nature 247:181-184.

List, R.J. 1966. Smithsonian Meteorological Tables. (Ed. 6, Reprint 3) Smith. Misc. Coll. 114:1-527.

Lynch, J.M., and N.J. Poole (Eds.). 1979. Microbial Ecology: A Conceptual Approach. Blackwell Scientific Publications, Oxford. 266 pp.

Mabey, W., and T. Mill. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. J. Phys. Chem. Ref. Data 7:383-415.

Malanchuk, J., J. Otis, and H. Bouver. 1980. Efficient Algorithms for Solving Systems of Ordinary Differential Equations for Ecosystem Modeling. U.S. Environmental Protection Agency, Athens, Georgia. EPA-600/3-80-037. 149 pp.

McCall, P.L., and J.B. Fisher. 1977. Vertical transport of sediment solids by Tubifex tubifex (Oligochaeta) (abstract). Proc. 20th Conf. Great Lakes Res., cited from Jones and Bowser 1978.

McCave, I.N. (Ed.) 1976. The Benthic Boundary Layer. Plenum Press, New York and London. 323 pp.

Mackay, D. 1978. Volatilization of pollutants from water. pp. 175-185 In: O. Hutzinger, I.H. van Lelyveld, and B.C.J. Zoeteman (Eds.) Aquatic Pollutants: Transformation and Biological Effects. Pergamon Press, Oxford.

Mackay, D. 1979. Finding fugacity feasible. Environ. Sci. Technol. 13:1218-1223.

Mackay, D., and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9:1178-1180.

Mackay, D., and A.W. Wolkoff. 1973. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 7:611-614.

Matsumura, F. 1972. Current pesticide situation in the United States. pp. 33-60 In: F. Matsumura, G.M. Boush, and T. Misato (Eds.) Environmental Toxicology of Pesticides. Academic Press, New York and London.

Matsumura, F., G.M. Boush, and T. Misato. (Eds.) 1972. Environmental Toxicology of Pesticides. Academic Press, New York and London. 637 pp.

Mickle, A.M., and R.G. Wetzel. 1978. Effectiveness of submersed angiosperm-epiphyte complexes on exchange of nutrients and organic carbon in littoral systems. II. Dissolved organic carbon. Aquat. Bot. 4:317-329.

Mill, T. 1980. Chemical and photo oxidation. pp. 77-105 In: O. Hutzinger (Ed.) The Handbook of Environmental Chemistry. Volume 2 Part A -- Reactions and Processes. Springer-Verlag, Berlin-Heidelberg-New York.

Mill, T., H. Richardson, and D.G. Hendry. 1978. Oxidation of organic compounds in aquatic systems: the free radical oxidation of cumene. pp. 223-236 In: O. Hutzinger, L.H. van Lelyveld, and B.C.J. Zoeteman. (Eds.) Aquatic Pollutants: Transformation and Biological Effects. Pergamon Press, Oxford.

Mill, T., D.G. Hendry, and H. Richardson. 1980. Free-radical oxidants in natural waters. Science 207:886-887.

Miller, G.C., and R.G. Zepp. 1979a. Effects of suspended sediments on photolysis rates of dissolved pollutants. Water Res. 13:453-459.

Miller, G.C., and R.G. Zepp. 1979b. Photoreactivity of aquatic pollutants sorbed on suspended sediments. Environ. Sci. Technol. 13:860-863.

Monod, J. 1942. Recherches sur la croissance des cultures bacteriennes. Herman et Cie, Paris.

Mulkey, L.A., and L.A. Burns. 1980. Toxic substances and small structure water quality management. Paper No. 80-2533, presented at the 1980 Winter Meeting, Amer. Soc. Agric. Eng., Dec. 1980.

Neely, W.B. 1980. Chemicals in the Environment: Distribution, Transport, Fate, Analysis. Marcel Dekker, Inc. New York and Basel. 245 pp.

Oliver, B.G., E.G. Cosgrove, and J.H. Carey. 1979. Effect of suspended sediments on the photolysis of organics in water. Environ. Sci. Technol. 13:1075-1077.

Paris, D.F., D.L. Lewis, and N.L. Wolfe. 1975. Rates of degradation of malathion by bacteria isolated from aquatic syste. Environ. Sci. Technol. 9:135-138.

Paris, D.F., W.C. Steen, G.L. Baughman, and J.T. Barnett, Jr. 1981. Second-order model to predict microbial degradation of organic compounds in natural waters. Appl. Environ. Microbiol. 41:603-609.

Peng, T.-H. 1973. Determination of gas exchange rates across sea-air interface by the radon method. Ph.D. Thesis, Columbia Univ. (cited from Emerson 1975)

Pirt, S.J. 1975. Principles of microbe and cell cultivation. Blackwell Scientific Publications, Oxford.

Platt, T., K.L. Denman, and A.D. Jassby. 1977. Modeling the productivity of phytoplankton. pp. 807-856 In: E.D. Goldberg, I.N. McCave, J.J. O'Brien, and J.H. Steele (Eds.) The Sea. Vol. 6: Marine Modeling. Wiley-Interscience, New York.

Poole, H.H., and W.R.G. Atkins. 1926. On the penetration of light into sea-water. J. Mar. biol. Ass. U.K. 14:177-198. (cited from Hutchinson 1957)

Priesendorfer, R.W. 1958a. Unified irradiance equations. Scripps Institute of Oceanography Report 58-43 (cited from Smith and Tyler 1976).

Priesendorfer, R.W. 1958b. Directly observable quantities for light fields in natural hydrosols. Scripps Institute of Oceanography Report 58-46 (cited from Smith and Tyler 1976).

Reid, R.C., J.M. Prausnitz, and T.K. Sherwood. 1977. The Properties of Gases and Liquids, 3rd Ed. McGraw-Hill Book Company, New York. 688 pp.

Rona, E. 1918. Diffusionsgrosse und Atomdurchmesser der Radium-emanation. Z. Physik. Chem. (Leipzig) 92:213-218. (cited from Emerson 1975)

Ross, R.D., and D.G. Crosby. 1975. The photooxidation of aldrin in water. Chemosphere 4:277-282.

Sanders, W.M. III. 1979. Exposure assessment: a key issue in aquatic toxicology. pp. 271-283 In: L.L. Marking and R.A. Kimerle (Eds.). Aquatic Toxicology. ASTM STP 667. American Society for Testing and Materials, Philadelphia.

Schindler, D.W. 1971. Light, temperature, and oxygen regimes of selected lakes in the Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Bd. Canada 28:157-169.

Schink, D.R., and N.L. Guinasso, Jr. 1977. Effects of bioturbation on sediment-seawater interaction. Marine Geol. 23:133-154.

Schuster, J.C. 1965. Canal discharge measurements with radioisotopes. J. Hydraul. Div. Proc. Am. Soc. Civ. Eng. 91:101-124. (cited from Fischer et al. 1979)

Schwarzenbach, R.P., E. Molnar-Kubica, W. Giger, and S.G. Wakeham. 1979. Distribution, residence time, and fluxes of tetrachloroethylene and 1,4-dichlorobenzene in Lake Zurich, Switzerland. Environ. Sci. Technol. 13:1367-1373.

Sherrill, T.W., and G.S. Sayler. 1980. Phenanthrene biodegradation in freshwater environments. Appl. Environ. Microbiol. 39:172-178.

Slater, J.H. 1979. Microbial population and community dynamics. pp. 45-63 In: J.M. Lynch and N.J. Poole (Eds.) Microbial Ecology: A Conceptual Approach. Blackwell Scientific Publications, Oxford.

Smith, J.H., W.R. Mabey, N. Bohonos, B.R. Holt, S.S. Lee, T.-W. Chou, D.C. Bomberger, and T. Mill. 1978. Environmental Pathways of Selected Chemicals in Freshwater Systems: Part II. Laboratory Studies. U.S. Environmental Protection Agency, Athens, Georgia. EPA-600/7-78-074. 406 pp.

Smith, J.H., D.C. Bomberger, Jr., and D.L. Haynes. 1980. Prediction of the volatilization rates of high-volatility chemicals from natural water bodies. Environ. Sci. Technol. 14:1332-1337.

Smith, R.C., and K.S. Baker. 1978a. The bio-optical state of ocean waters and remote sensing. Limnol. Oceanogr. 23:247-259.

Smith, R.C., and K.S. Baker. 1978b. Optical classification of natural waters. Limnol. Oceanogr. 23:260-267.

Smith, R.C., and K.S. Baker. 1979. Penetration of UV-B and biologically effective dose-rates in natural waters. Photochem. Photobiol. 29:311-323.

Smith, R.C., and K.S. Baker. 1981. Optical properties of the clearest natural waters (200-800 nm). Applied Optics 20:177-184.

Smith, R.C., and J.E. Tyler. 1976. Transmission of solar radiation into natural waters. Photochem. Photobiol. Rev. 1:117-155.

Snodgrass, W.J. 1977. Relationship of vertical transport across the thermocline to oxygen and phosphorus regimes: Lake Ontario as a prototype. pp. 179-202 In: R.J. Gibbs (Ed.) Transport Processes in Lakes and Oceans. Plenum Press, New York and London.

Strickler, S.J., and R.A. Berg. 1962. Relationship between absorption intensity and fluorescence lifetime of molecules. J. Chem. Phys. 37: 814-822.

Stuart, F. 1970. FORTRAN Programming. John Wiley and Sons, Inc., New York. 371 pp.

Stumm, W., and J.J. Morgan. 1970. Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters. Wiley-Interscience, New York. 583 pp.

Swisher, R.D. 1970. Surfactant Biodegradation. Marcel Dekker, Inc., New York. 496 pp.

Talling, J.F., R.B. Wood, M.V. Prosser, and R.M. Baxter. 1973. The upper limit of photosynthetic productivity by phytoplankton: Evidence from Ethiopian soda lakes. Freshwat. Biol. 3:53-76.

Tinsley, I.J. 1979. Chemical Concepts in Pollutant Behavior. John Wiley and Sons, New York-Chichester-Brisbane-Toronto. 265 pp.

Tsivoglou, E.C. 1967. Tracer Measurement of Stream Reaeration. Fed. Water Poll. Contr. Admin., Washington, D.C. 204 pp.

Tsivoglou, E.C., M.A. McClanahan, and W.M. Sanders, III. (Eds.) 1972. Proceedings of a Symposium on Direct Tracer Measurement of the Reaeration Capacity of Streams and Estuaries. U.S. Environmental Protection Agency, Washington, D.C. Water Pollution Control Research Series 16050 FOR 01/72. 194 pp.

Turro, N.J. 1978. Modern Molecular Photochemistry. The Benjamin/Cummings Publ. Co., Inc., Menlo Park, California. 628 pp.

Vanderborght, J.P., and R. Wollast. 1977. Mass transfer properties in sediments near the benthic boundary layer. pp. 209-219 In: J.C.J. Nihoul (Ed.) Bottom Turbulence. Proceedings of the 8th International Liege Colloquium on Ocean Hydrodynamics. Elsevier Scientific Publishing Co., Amsterdam. 306 pp.

Visser, S.A., G. Lamontagne, V. Zoulalian, and A. Tessier. 1977. Bacteria active in the degradation of phenols in polluted waters of the St. Lawrence River. Arch. Environm. Contam. Toxicol. 6:455-469.

Vivian, J.E., and C.J. King. 1964. AIChE J. 10:220 (cited from Reid, Prausnitz, and Sherwood 1977)

Weast, R.C. (Ed.) 1971. Handbook of Chemistry and Physics. 51st edition. The Chemical Rubber Co., Cleveland.

Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia. 743 pp.

Whitman, R.G. 1923. A preliminary experimental confirmation of the two-film theory of gas absorption. Chem. Metallurg. Eng. 29:146-148.

Wilhelm, E., R. Battino, and R.J. Wilcock. 1977. Low-pressure solubility of gases in liquid water. Chem. Rev. 77:219-262.

Wolfe, N.L. 1980. Determining the role of hydrolysis in the fate of organics in natural waters. pp. 163-178 In: R. Haque (Ed.) Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. Ann Arbor Science Publishers, Ann Arbor.

Wolfe, N.L., L.A. Burns, and W.C. Steen. 1980. Use of linear free energy relationships and an evaluative model to assess the fate and transport of phthalate esters in the aquatic environment. Chemosphere 9:393-402.

Wolfe, N.L., W.C. Steen, and L.A. Burns. 1980. Phthalate ester hydrolysis: linear free energy relationships. Chemosphere 9:403-408.

Wolfe, N.L., R.G. Zepp, J.A. Gordon, G.L. Baughman, and D.M. Cline. 1977. Kinetics of chemical degradation of malathion in water. Environ. Sci. Technol. 11:88-93.

Yotsukura, N., H.B. Fischer, and W.W. Sayre. 1970. Measurement of Mixing Characteristics of the Missouri River between Sioux City, Iowa and Plattsmouth, Nebraska. U.S. Geological Survey Water-Supply Paper 1899-G. (cited from Fischer et al. 1979)

Zepp, R.G. 1978. Quantum yields for reaction of pollutants in dilute aqueous solution. Environ. Sci. Technol. 12:327-329.

Zepp, R.G. 1980. Assessing the photochemistry of organic pollutants in aquatic environments. pp. 69-110 In: R. Haque (Ed.) Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. Ann Arbor Science Publishers, Ann Arbor.

Zepp, R.G., and G.L. Baughman. 1978. Prediction of photochemical transformation of pollutants in the aquatic environment. pp. 237-263 In: O. Hutzinger, I.H. van Lelyveld, and B.C.J. Zoeteman (Eds.) Aquatic Pollutants: Transformation and Biological Effects. Pergamon Press, Oxford.

Zepp, R.G., and D.M. Cline. 1977. Rates of direct photolysis in aquatic environment. Environ. Sci. Technol. 11:359-366.

Zepp, R.G., N.L. Wolfe, L.V. Azarraga, R.H. Cox, and C.W. Pape. 1977. Photochemical transformation of the DDT and methoxychlor degradation products, DDE and DMDE, by sunlight. Arch. Environm. Contam. Toxicol. 6:305-314.

Zepp, R.G., N.L. Wolfe, G.L. Baughman, and R.C. Hollis. 1977. Singlet oxygen in natural waters. Nature 267:421-423.

Zepp, R.G., N.L. Wolfe, J.A. Gordon, and G.L. Baughman. 1975. Dynamics of 2,4-D esters in surface waters: hydrolysis, photolysis, and vaporization. Environ. Sci. Technol. 9:1144-1150.

Zepp, R.G., N.L. Wolfe, J.A. Gordon, and R.C. Fincher. 1976. Light-induced transformations of methoxychlor in aquatic systems. J. Agric. Food Chem. 24:727-733.

GLOSSARY FOR EXAMS' COMPUTATIONAL SUBROUTINES

This glossary contains an alphabetical listing of all COMMON variables of EXAMS' computational subroutines. For each variable, this glossary gives:

> Name of the variable
> Location (e.g., labeled common XXXX)
> Data type: Real (R), Integer (I), or Logical (L)
> Dimension type: Scalar (S), Vector (V), or Matrix (M)
> Numerical size of dimensions (e.g., (39,5))
> Definition of the variable
> Units (as a separate line in the case of input variables)
> List of computational subroutines requiring the variable

Input variables can also be identified by the terminal letter in the variable name (G for Global, e.g., VOLG). All variables that include a vector dimension determined by the maximum number of compartments available to define a system are designated "NPX."

ABSG(39,5) in labeled common DPHOTG (R,M)
Absorption spectrum (molar extinction coefficients) for each (of 5 possible) ionic species of the chemical, average values over each of 39 wavelength intervals. The 39 wavelength intervals are defined in Table 2.18 (Section 2.3.3).

ABSG(I,1) -- absorption spectrum of neutral molecule (SH2)
ABSG(I,2) -- absorption spectrum of singly charged cation (SH3+)
ABSG(I,3) -- absorption spectrum of doubly charged cation (SH4++)
ABSG(I,4) -- absorption spectrum of singly charged anion (SH-)
ABSG(I,5) -- absorption spectrum of doubly charged anion (S=)

Units: /cm/(mole/Liter) (decadic)
Subroutines: FIRORD, PHOTO2, PRCHEM

ACBACG(NPX) in labeled common QUALG (R,V)
Proportion of bacterial population that actively degrades synthetic organic chemical. If the biolysis rate constants are not based on natural mixed bacterial populations, the total bacterial populations (BACTOG) given for each compartment can be modified (via ACBACG) to give the size of the population that is actively degrading the chemical.

Units: dimensionless ratio, nominal range 0.0 to 1.0
Subroutines: FIRORD, PRENV

ADVPRG(3*NPX) in labeled common SETUPG (R,V)
Proportion of total advective flow leaving compartment JFRADG that is delivered to compartment ITOADG. Although usually 1.0, this feature allows for downstream branching, loop flows, etc. An error condition is raised if the ADVPRGs for a given compartment sum to neither 0 nor 1.
Units: dimensionless
Subroutines: PRENV, WATADV

AECG(NPX) in labeled common SEDMG (R,V)
Anion exchange capacity of sediments in each compartment. This parameter is useful in relating sediment sorption (partitioning) of anions to a variable characteristic of system sediments.
Units: milliequivalents/100 grams dry weight
Subroutines: DISTRB, PRENV

ALPHA(18,NPX) in labeled common PARTIL (R,M)
The 18 values of ALPHA are distribution coefficients (fraction of total concentration of chemical (Y) present as a particular species/form configuration of the molecule), for each ecosystem compartment. Each ALPHA vector allows for partitioning among 5 chemical species (neutral molecule, singly or doubly charged anions and cations), with each species potentially partitioned among 3 physical forms (dissolved, sediment-sorbed, biosorbed). The 3 remaining elements in the vector are used for the total dissolved, sediment-sorbed, and bio-sorbed distribution coefficients.

ALPHA(1,J) -- fraction of chemical present as the neutral molecule (SH2) dissolved in the water phase of the compartment.

ALPHA(2,J) -- fraction present as neutral molecule sorbed with sediment phase of compartment.

ALPHA(3,J) -- fraction present as neutral molecule sorbed with compartment biomass.

ALPHA(4,J) -- fraction of chemical present as dissolved singly charged cation generated by base dissociation or

$$SH2 + H2O \longleftrightarrow SH3^{+} + OH^{-}$$

in the water phase of the compartments.

ALPHA(5,J) -- fraction of chemical present as SH3+ sorbed with sediment phase of compartment.

ALPHA(6,J) -- fraction of chemical present as biosorbed SH3+.

ALPHA(7,J) -- fraction of chemical present as a dissolved, doubly charged cation (SH4++) via base dissociation or

SH3+ + H2O <---> SH4++ + OH-

in the water phase of each compartment.

ALPHA(8,J) -- fraction of chemical present as SH4++ sorbed with sediment phase of compartment J.

ALPHA(9,J) -- fraction of chemical present as biosorbed SH4++ in compartment J.

ALPHA(10,J) -- fraction present as singly charged anion (SH-) produced from organic acid via

SH2 + H2O <---> H3O+ + SH-

dissolved in water phase of compartment J.

ALPHA(11,J) -- fraction present as SH- sorbed with sediments

ALPHA(12,J) -- fraction present as biosorbed SH-.

ALPHA(13,J) -- fraction of chemical concentration present as doubly charged anion dissolved in water phase of compartment J, produced by

SH- + H2O <---> H3O+ + S=

ALPHA(14,J) -- fraction present as S= sorbed to sediment phase J.

ALPHA(15,J) -- fraction present as biosorbed S=.

ALPHA(16,J) -- fraction of total concentration present in dissolved form in the water phase of compartment J. Sum of ALPHA(1,J) + ALPHA(4,J) + ALPHA(7,J) + ALPHA(10,J) + ALPHA(13,J).

ALPHA(17,J) -- fraction of total concentration present as sediment-sorbed molecules in compartment J. Sum of ALPHA(2,J) + ALPHA(5,J) + ALPHA(8,J) + ALPHA(11,J) + ALPHA(14,J).

ALPHA(18,J) -- fraction of total concentration present as biosorbed species of the chemical. Sum of ALPHA((3, 6, 9, 12, 15), J).

Subroutines: AVEOUT, DISPER, DISTRB, FIRORD, OUTP, STEADY

AREAG(NPX) in labeled common GEOMT (R,V)
Area of ecosystem elements (compartments). This variable is used

(inter alia) to convert steady-state masses of chemical captured in each compartment to a grams/square meter basis. For (E)pilimnion and (L)ittoral compartments, AREAG(J) is the area of the air-water interface; for (H)ypolimnion compartments AREAG is the area of the thermocline; for (B)enthic compartments it is the surface area of the bottom. In the latter case AREAG may differ from XSTURG in a dispersive exchange pair because of a reduction in exchanging area due to rock outcrops, etc.
Units: square meters
Subroutines: AVEOUT, DISTRB, FLOWS, OUTP, PRENV, VOLAT

B in labeled common SETUPL (I,S)
Letter code for detecting (B)enthic compartments.
Subroutines: BLOCK DATA, DISTRB, GHOST, FIRORD, FLOWS, PRENV

BATCH in labeled common SETUPG (I,S)
Flag for indicating batch vs. interactive control. Batch mode is denoted by BATCH set to 1; interactive mode by BATCH set to 0.
Computational subroutines: BLOCK DATA, PRCHEM, PRENV, STEADY
Interactive subroutines: LISSTR, MAIN, SHOW

BACTOG(NPX) in labeled common QUALG (R,V)
Bacterial population density in each compartment.
Units: Water column compartments: cells/milliliter
Benthic compartments: cells/100 grams dry weight of sediment
Subroutines: FIRORD, PRENV

BIOLKL(NPX) in labeled common CHEM1L (R,V)
Total pseudo-first-order degradation rate constant (/hr) for bacterial biolysis in each compartment.
Subroutines: FIRORD, FLXOUT

BIOMSG(NPX) in labeled common QUALG (R,V)
Total actively sorbing biomass in each ecosystem compartment. This parameter is used in computation of sorption of the chemical with plant/animal material in the ecosystem compartments. The parameter is interpreted differently for the water column vs. the benthic compartments. For a water column compartment, total biomass must be expressed as mg (dry weight)/Liter of water in the compartment, and it may include all biomass subject to biosorptive exchange with that water -- i.e., plankton plus benthic algae, macrophyte leaves, etc. Parameter PLRAG (the PLankton RAtio) gives the fraction of this total biomass that is passively transported by advective and dispersive water movement. In the case of benthic compartments, BIOMSG is the total biomass of the benthic infauna etc. in grams (dry weight) per square meter of bottom. Once again the PLRAG for each (B)enthic

compartment indicates that fraction of the biomass that is not firmly fixed in the bottom, but can be transported by turbulent and advective motions -- thus distinguishing, for example, plant roots and bivalves from smaller creatures such as planaria or amphipods.
Units: Water column compartments: mg (dry weight)/Liter
Benthic compartments: grams (dry weight)/square meter
Subroutines: DISTRB, PRENV

BIOPCT in labeled common RESLT (R,S)
Percentage of total chemical load on the system that is consumed via biolysis at steady state.
Subroutines: FLXOUT, SUMUP

BIOTMG(NPX) in labeled common QUALG (R,V)
Biotemperature in each ecosystem compartment, i.e., temperature to be used in conjunction with Q-10 expressions for biolysis rate constants. This parameter is separated from the physical temperature input data (TCELG) in order that the input data can reflect Q-10 averaging of an observed temperature time-series.
Units: degrees C.
Subroutines: FIRORD, PRENV

BIOTOL(NPX) in labeled common MASSL (R,V)
Compartment biomasses converted to internal units (kg (dry) per liter of water content).
Subroutines: AVEOUT, DISTRB, OUTP

BOTLAM(39) in labeled common ENPARL (R,V)
On entrance to subroutine PHOTO2, BOTLAM holds the spectral irradiance at the bottom of the last previous ecosystem compartment evaluated by the routine. On exit from PHOTO2, BOTLAM contains the spectral irradiance at the bottom of the current water column compartment.
Subroutines: PHOTO2

BOTLIT in labeled common ENPARL (R,S)
On entrance to subroutine PHOTO1, BOTLIT contains the relative (to surface light) light intensity at the bottom of the last previous water-column compartment evaluated by the routine. On exit from PHOTO1, BOTLIT contains the relative light intensity at the bottom of the current compartment.
Subroutines: PHOTO1

CECG(NPX) in labeled common SEDMG (R,V)
Cation exchange capacity of sediments in each compartment. This

parameter is of utility in relating sediment sorption (partitioning) of cations to a variable characteristic of system sediments.
Units: milliequivalents/100 grams dry weight of sediment
Subroutines: DISTRB, PRENV

CHARLG(3*NPX) in labeled common SETUPG (R,V)
Characteristic length (average of compartment dimensions or mixing lengths) for the dispersive exchange pairing given by the corresponding compartment numbers of JTURBG and ITURBG. A given compartment may have different mixing lengths in different exchange pairings.
Units: meters
Subroutines: DISPER, PRENV

CHEMNA(60) in labeled common NAME1G (input data) (I,V)
CHEMNA holds the name of the synthetic organic chemical, with up to 60 characters permitted. CHEMNA is used in the headings for the data written to the output files of the program.
Units: Alphameric characters
Subroutines: AVEOUT, FIRORD, FLXOUT, GHOST, PRCHEM, PRENV

CHEMPC in labeled common RESLT (R,S)
Percentage of total chemical load on the system that is consumed via all chemical transformation processes at steady state.
Subroutines: FLXOUT, SUMUP

CHLG(NPX) in labeled common PHOG (R,V)
Concentration of chlorophyll and chlorophyll-like pigments in water column compartments. (Dummy variable in benthic compartments.)
Units: milligrams/Liter
Subroutines: PHOTO2, PRENV

CLOUDG in labeled common PHOG (R,S)
Average cloudiness in tenths of full sky cover.
Units: dimensionless, range of 0.0 to 10.0
Subroutines: PHOTO1, PHOTO2, PRENV

CMPETG(NPX) in labeled common PHOG (R,V)
Single-valued zenith light extinction coefficient for water columns, dummy variable for benthic compartments.
Units: /meter
Subroutines: PHOTO1, DATAIN

CONLDL(NPX) in labeled common MISCL (R,V)
Numerical rate of increase (mg/L/hr) of chemical concentration in each compartment as a result of external loadings.
Subroutines: FIRORD, STEADY

DEPTHG(NPX) in labeled common GEOMT (R,V)
Average depth of each compartment.
Units: meters
Subroutines: PHOTO1, PHOTO2, PRENV

DFACG(NPX) in labeled common PHOG (R,V)
Distribution function (ratio of optical path length to vertical depth) for each compartment. (Dummy variable for benthic sediments.)
Units: dimensionless, values constrained to range of 1.0 to 2.0
Subroutines: PHOTO1, PHOTO2, PRENV

DOCETA(39) in labeled common DPHOTL (R,V)
Spectral light absorption coefficients (/m/(mg/L)) for dissolved organic carbon. Values and data sources given in Section 2.3.3.
Subroutines: BLOCK DATA, PHOTO2, PRENV

DOCG(NPX) in labeled common PHOG (R,V)
Dissolved organic carbon concentration in water column compartments. (Dummy variable for benthic compartments.)
Units: mg/Liter
Subroutines: PHOTO2, PRENV

DOMAX(10) in labeled common RESLT (R,V)
Storage locations for maximum values at steady-state.

DOMAX(1) -- maximum value of Z(11) in the water column
DOMAX(2) -- maximum value of Z(7) in the water column
DOMAX(3) -- maximum value of Z(8) in the water column
DOMAX(4) -- maximum value of Z(9) in the water column
DOMAX(5) -- maximum value of Z(10) in the water column
DOMAX(6) -- maximum value of Z(11) in the bottom sediments
DOMAX(7) -- maximum value of Z(7) in the bottom sediments
DOMAX(8) -- maximum value of Z(8) in the bottom sediments
DOMAX(9) -- maximum value of Z(9) in the bottom sediments
DOMAX(10) -- maximum value of Z(10) in the bottom sediments

Subroutines: AVEOUT, SUMUP

DOMIN(10) in labeled common RESLT (R,V)
Storage locations for minimum values at steady-state.

DOMIN(1) -- minimum value of Z(11) in the water column
DOMIN(2) -- minimum value of Z(7) in the water column
DOMIN(3) -- minimum value of Z(8) in the water column
DOMIN(4) -- minimum value of Z(9) in the water column
DOMIN(5) -- minimum value of Z(10) in the water column
DOMIN(6) -- minimum value of Z(11) in the bottom sediments
DOMIN(7) -- minimum value of Z(7) in the bottom sediments
DOMIN(8) -- minimum value of Z(8) in the bottom sediments
DOMIN(9) -- minimum value of Z(9) in the bottom sediments
DOMIN(10) -- minimum value of Z(10) in the bottom sediments

Subroutines: AVEOUT

DRFLDG(NPX) in labeled common LOADSG (R,V)
Drift loadings (aerial drift, direct applications, stack fallout, etc.) of chemical on each system element.
Units: kg/hour
Subroutines: CKLOAD, STEADY

DSPG(3*NPX) in labeled common SETUPG (R,V)
Eddy diffusivity to be applied to the dispersive exchange pairing given by the corresponding compartment numbers of JTURBG and ITURBG. In the case of horizontal mixing DSPG is the longitudinal dispersion coefficient, for vertical mixing it may represent exchange across the thermocline or exchanges with bottom sediments. In the latter case DSPG is a composite of direct sorption to the sediment surface, mixing of the sediments by benthic animals, stirring by demersal fishes, etc.
Units: square meters/hour
Subroutines: DISPER, PRENV

E in labeled common SETUPL (I,S)
Letter code for detecting (E)pilimnion compartments.
Subroutines: BLOCK DATA, DISTRB, FLOWS, GHOST, PHOTO1, PHOTO2

EAHG(3,5) in labeled common HYDROG (R,M)
Arrhenius activation energy of specific-acid-catalyzed hydrolysis of the chemical. Matrix indices allow entry of the data as separate values for each chemical species/physical form configuration of the molecule.

EAHG(1,1) -- datum applicable to dissolved SH2
EAHG(2,1) -- datum applicable to sediment-sorbed SH2
EAHG(3,1) -- datum applicable to biosorbed SH2
EAHG(1,2) -- datum applicable to dissolved SH3+
EAHG(2,2) -- datum applicable to sediment-sorbed SH3+
EAHG(3,2) -- datum applicable to biosorbed SH3+
EAHG(1,3) -- datum applicable to dissolved SH4++

EAHG(2,3) -- datum applicable to sediment-sorbed SH4++
EAHG(3,3) -- datum applicable to biosorbed SH4++
EAHG(1,4) -- datum applicable to dissolved SH-
EAHG(2,4) -- datum applicable to sediment-sorbed SH-
EAHG(3,4) -- datum applicable to biosorbed SH-
EAHG(1,5) -- datum applicable to dissolved S=
EAHG(2,5) -- datum applicable to sediment-sorbed S=
EAHG(3,5) -- datum applicable to biosorbed S=

Units: kcal/gram mole
Subroutines: FIRORD, PRCHEM

EBHG(3,5) in labeled common HYDROG (R,M)
Arrhenius activation energy of specific-base-catalyzed hydrolysis of the chemical. Matrix indices allow entry of the data as separate values for each chemical species/physical form configuration of the molecule. The 15 species/form indices are given as part of the definition of EAHG above.
Units: kcal/gram mole
Subroutines: FIRORD, PRCHEM

EHENG in labeled common VOLATG (R,S)
Parameter used to compute Henry's law constants as a function of environmental temperatures (TCELG). When EHENG is non-zero, the Henry's law constant is computed as follows:

log HENRY = HENRYG-((1000.*EHENG)/(4.58*(TCELG+273.15)))

Units: kcal/gram mole
Subroutines: PRCHEM, VOLAT

ENHG(3,5) in labeled common HYDROG (R,M)
Arrhenius activation energy of neutral hydrolysis of the chemical. Matrix indices allow entry of the data as separate values for each chemical species/physical form configuration of the molecule. The 15 species/form indices are given as part of the definition of EAHG above.
Units: kcal/gram mole
Subroutines: FIRORD, PRCHEM

EOXG(3,5) in labeled common OXIDG (R,M)
Arrhenius activation energy of oxidative transformation of the chemical. Matrix indices allow entry of the data as separate values for each chemical species/physical form configuration of the molecule. The 15 species/form indices are given as part of the definition of EAHG above.
Units: kcal/gram mole
Subroutines: FIRORD, PRCHEM

EPKAG(2) in labeled common IONG (R,V)
Exponential term (see PKAG) for acid dissociation constants of chemical (Ka). EPKAG(1) is datum for generation of SH- from SH2; EPKAG(2) is datum for generation of S= from SH-.
Units: kcal/gram mole
Subroutines: DISTRB, PRCHEM

EPKBG(2) in labeled common IONG (R,V)
Exponential term (see PKBG) for base dissociation constants of chemical (Kb). EPKBG(1) is datum for generation of SH3+ from SH2; EPKBG(2) is datum for generation of SH4++ from SH3+.
Units: kcal/gram mole
Subroutines: DISTRB, PRCHEM

ESOLG(5) in labeled common PCHEMG (R,V)
Exponential term for describing solubility of the chemical as a function of temperature (see SOLG).

ESOLG(1) -- datum for solubility of SH2
ESOLG(2) -- datum for solubility of SH3+
ESOLG(3) -- datum for solubility of SH4++
ESOLG(4) -- datum for solubility of SH-
ESOLG(5) -- datum for solubility of S=

Units: kcal/gram mole
Subroutines: CKLOAD, PRCHEM, VOLAT

EVAPG(NPX) in labeled common CLIMG (R,V)
Evaporative water losses from ecosystem compartments.
Units: millimeters/month
Subroutines: FLOWS, PRENV

EVAPL(NPX) in labeled common FLOWSL (R,V)
Evaporative water losses converted to internal units (L/hr).
Subroutines: FLOWS

EVPRG in labeled common VOLATG (R,S)
Molar heat of vaporization for vapor pressure described as a function of temperature (see VAPRG).
Units: kcal/gram mole
Subroutines: PRCHEM, VOLAT

EXPOKL(NPX) in labeled common CHEMIL (R,V)
Pseudo-first-order rate constant (/hr) expressing rate of decrease of chemical concentration in each compartment resulting from entrained exports of chemical leaving the system.

Subroutines: FIRORD, FLXOUT

EXPPCT in labeled common RESLT (R,S)
Percent of total chemical load that is exported from the system at steady state.
Subroutines: FLXOUT, SUMUP

FROCG(NPX) in labeled common SEDMG (R,V)
Organic carbon content of compartment sediments as fraction of dry weight. Parameter is coupled to KOCG to generate the sediment partition coefficient for SH2 as a function of a property (FROCG) of the sediment.
Units: dimensionless weight ratio
Subroutines: DISTRB, PRENV

H in labeled common SETUPL (I,S)
Letter code for detecting (H)ypolimnion compartments.
Subroutines: BLOCK DATA, DISTRB, FIRORD, FLOWS, GHOST, PHOTO1, PHOTO2

HENRYG in labeled common VOLATG (R,S)
Henry's law constant of the chemical. If parameter EHENG is non-zero, HENRYG is used as the pre-exponential factor in computing the Henry's law constant as a function of environmental temperatures (TCELG).
Units: atmosphere-cubic meters/mole
Subroutines: FIRORD, PRCHEM, VOLAT

HYDRKL(NPX) in labeled common CHEM1L (R,V)
Total pseudo-first-order rate constant (/hr) for hydrolytic transformations of the chemical in each compartment.
Subroutines: FIRORD, FLXOUT

ICALL in labeled common SETUPL (I,S)
ICALL is an internal flag used in subroutine PHOTO2 to indicate that the surface light field has been filled out to full wavelength intervals and pre-multiplied by a numerical conversion factor.
Subroutines: GHOST, PHOTO2

IFLAG in labeled common TIMEL (internal variable) (I,S)
IFLAG is an internal program monitoring flag. It is used to control subsequent operations when any of a number of error conditions are encountered.
Subroutines: CKLOAD, DISTRB, DRIVER, FLOWS, GHOST, PRENV,

SEDADV, STEADY, SUMUP, WATADV

IFLLDG(NPX) in labeled common LOADSG (R,V)
Chemical loadings entering the system via interflows (all subsurface water flows entering via a sediment compartment).
Units: kilograms/hour
Subroutines: CKLOAD, STEADY

INDEXS(NPX) in labeled common SETUPL (I,V)
INDEXS is a vector of flags designating benthic compartments. INDEXS is 1 for (B)enthic sediments, 0 otherwise.
Subroutines: AVEOUT, DISPER, DISTRB, FIRORD, FLXOUT, OUTP, SEDADV

INDEXW(NPX) in labeled common SETUPL (I,V)
INDEXW is a vector of flags designating water column compartments. It takes a value of 1 for E, H, and L compartments and a value of 0 for B compartments.
Subroutines: AVEOUT, DISPER, DISTRB, FIRORD, FLOWS

INTFL(NPX) in labeled common FLOWSL (R,V)
Compartment interflows converted to internal units (liters/hr).
Subroutines: CKLOAD, FLOWS

INTFLG(NPX) in labeled common FLOWG (R,V)
Interflow (subsurface water flow) entering each ecosystem compartment. Assumed to involve a flow of water only, usually entering the system via a sediment compartment.
Units: cubic meters/hour
Subroutines: FLOWS, PRENV

INTINL(NPX,NPX) in labeled common CHEM1L (R,M)
Matrix of pseudo-first-order coefficients (/hr) expressing rate of increase of chemical concentration in receiving compartments due to internal flows of water, sediments, and plankton among ecosystem compartments.
Subroutines: FCT, FDER, FIRORD, STEADY

ITOADG(3*NPX) in labeled common SETUPG (I,V)
Index vector containing compartment numbers designating the compartments to receive advective flow from the compartment occupying the corresponding position in vector JFRADG (i.e., ITOADG(K) and JFRADG(K) define an advective transport pathway of the system). (0,0) pairs are interpreted as empty storage locations, i.e., inactive pathways. ITOADG can contain a 0

paired with a non-zero value in JFRADG to indicate an export pathway. If the program encounters a compartment number greater than KOUNT (the number of compartments used to define the system), an error condition is raised. (See also ADVPRG, JFRADG.)
Units: dimensionless integer number
Subroutines: WATADV, PRENV

ITURBG(3*NPX) in labeled common SETUPG (I,V)
Index vector containing compartment numbers that, with the compartment number found at the corresponding location of JTURBG, define a dispersive transport pathway of the system. (0,0) pairs are interpreted as inactive pathways. A 0 in ITURBG paired with a non-zero compartment number in JTURBG is interpreted as a boundary condition with a clean (zero synthetic chemical) water-body. If the program encounters a compartment number greater than KOUNT (the number of compartments used to define the system), an error condition is raised. (See also CHARLG, DSPG, JTURBG, and XSTURG.)
Units: dimensionless integer number
Subroutines: DISPER, PRENV

JFRADG(3*NPX) in labeled common SETUPG (I,V)
Index vector containing compartment numbers designating the compartments that export via advective flows to the compartment occupying the corresponding position in vector ITOADG (i.e., ITOADG(K) and JFRADG(K) define an advective transport pathway of the system). (0,0) pairs are interpreted as empty storage locations, i.e., inactive pathways. JFRADG must not contain any zeros paired with non-zero compartment numbers in vector ITOADG, since chemical loadings to the system are handled explicitly as stream loads (STRLDG), non-point-source loadings (NPSLDG), etc. If the program encounters a compartment number greater than KOUNT (the number of compartments used to define the system), an error condition is raised. (See also ADVPRG, ITOADG.)
Units: dimensionless integer number
Subroutines: FLOWS, WATADV, PRENV

JSAV1 in labeled common SETUPL (I,S) Flag used in subroutine PHOTO1 to indicate that light extinction in the current compartment has already been computed.
Subroutines: GHOST, PHOTO1

JSAV2 in labeled common SETUPL (I,S)
Flag used in subroutine PHOTO2 to indicate that average spectral irradiance in the current compartment has already been computed.
Subroutines: GHOST, PHOTO2

JTURBG(3*NPX) in labeled common SETUPG (I,V)
Index vector containing compartment numbers that, with the compartment number found at the corresponding location of ITURBG, define a dispersive transport pathway of the system. (0,0) pairs are interpreted as inactive pathways. A 0 in JTURBG paired with a non-zero compartment number in ITURBG is interpreted as a boundary condition with a clean (zero synthetic chemical) water-body. If the program encounters a compartment number greater than KOUNT (the number of compartments used to define the system), an error condition is raised. (See also CHARLG, DSPG, and XSTURG.)
Units: dimensionless integer number
Subroutines: DISPER, PRENV

KA1L(NPX) in labeled common CHEM2L (R,V)
Local (computed) value of first acid dissociation constant (as a function of temperature when input data permits) of chemical in each system compartment.
Subroutines: CKLOAD, DISTRB

KA2L(NPX) in labeled common CHEM2L (R,V)
Local (computed) value of second acid dissociation constant (as a function of temperature when input data permits) of chemical in each system compartment.
Subroutines: CKLOAD, DISTRB

KAECG(2) in labeled common PARTG (R,V)
Multiplication of the anion exchange capacity of system sediments by KAECG gives the partition coefficient for sorption of the SH- anion (KAECG(1)) and the S= anion (KAECG(2)) to system sediments as a function of a property of the sediment. Inclusion of this feature is somewhat speculative at this time, but sorption characteristics of chemical ions can alternatively be loaded via KPSG.
Units: ((mg/kg)/(mg/L))/(meq/100 g dry weight)
Subroutines: DISTRB, PRCHEM

KAHG(3,5) in labeled common HYDROG (R,M)
Second-order rate constants for specific-acid-catalyzed hydrolysis of chemical. If the corresponding entry in the Arrhenius activation energy matrix (EAHG) for this reaction is zero, the value entered in KAHG is taken as the second-order rate constant. If the corresponding entry in the activation energy matrix (EAHG) is non-zero, the value entered in matrix KAHG is interpreted as the base-10 logarithm of the frequency factor in an Arrhenius function for the reaction, and local values of the second-order rate constant are computed as a function of temperature (TCELG) in each system compartment. The matrix

indices for each of the 15 possible chemical species/physical form configurations of the molecule are given in the text describing matrix EAHG.
Units: /mole[H+]/hour
Subroutines: FIRORD, PRCHEM

KB1L(NPX) in labeled common CHEM2L (R,V)
Local (computed) value of first base dissociation constant (as a function of temperature when input data permits) of chemical in each system compartment.
Subroutines: CKLOAD, DISTRB

KB2L(NPX) in labeled common CHEM2L (R,V)
Local (computed) value of second base dissociation constant (as a function of temperature when input data permits) of chemical in each system compartment.
Subroutines: CKLOAD, DISTRB

KBACSG(3,5) in labeled common BACTG (R,M)
Second-order rate constants for benthic sediment bacterial biolysis of the organic chemical. If the corresponding entry in the Q-10 matrix (QTBASG) for this process is zero, the number entered in matrix KBACSG is taken as the second-order rate constant. If the corresponding entry in the Q-10 matrix is non-zero, the value entered in matrix KBACSG is interpreted as the numerical value of the second-order rate constant at 20 degrees C., and local values of the rate constant are computed as a function of temperature (BIOTMG) in each ecosystem compartment. The matrix indices for each of the 15 possible chemical species/physical form configurations of the molecule are given in the text describing matrix EAHG.
Units: ml/cell/hour
Subroutines: FIRORD, PRCHEM

KBACWG(3,5) in labeled common BACTG (R,M)
Second-order rate constants for water column bacterial biolysis of the organic chemical. If the corresponding entry in the Q-10 matrix (QTBAWG) for this process is zero, the number entered in matrix KBACWG is taken as the second-order rate constant. If the corresponding entry in the Q-10 matrix is non-zero, the value entered in matrix KBACWG is interpreted as the numerical value of the second-order rate constant at 20 degrees C., and local values of the rate constant are computed as a function of temperature (BIOTMG) in each ecosystem compartment. The matrix indices for each of the 15 possible chemical species/physical form configurations of the molecule are given in the text describing matrix EAHG.
Units: ml/cell/hour

Subroutines: FIRORD, PRCHEM

KBHG(3,5) in labeled common HYDROG (R,M)
Second-order rate constants for specific-base-catalyzed hydrolysis of chemical. If the corresponding entry in the Arrhenius activation energy matrix (EBHG) for this reaction is zero, the value entered in KBHG is taken as the second-order rate constant. If the corresponding entry in the activation energy matrix (EBHG) is non-zero, the value entered in matrix KBHG is interpreted as the base-10 logarithm of the frequency factor in an Arrhenius function for the reaction, and local values of the second-order rate constant are computed as a function of temperature (TCELG) in each system compartment. The matrix indices for each of the 15 possible chemical species/physical form configurations of the molecule are given in the text describing matrix EAHG.
Units: /mole[OH-]/hour
Subroutines: FIRORD, PRCHEM

KCECG(2) in labeled common PARTG (R,V)
Multiplication of the cation exchange capacity of system sediments by KCECG gives the partition coefficient for sorption of the SH3+ cation (KCECG(1)) and the SH4++ cation (KCECG(2)) to system sediments as a function of a property of the sediment. Inclusion of this feature is somewhat speculative at this time, but sorption characteristics of chemical ions can alternatively be loaded via KPSG.
Units: ((mg/kg)/(mg/L))/(meq/100 g dry weight)
Subroutines: DISTRB, PRCHEM

KDPG(5) in labeled common DPHOTG (R,V)
KDPG(K) is a near-surface photolytic rate constant for the Kth ionic species of the chemical. The ionic species denoted by each value of K is given in the text describing parameter ESOLG. Each value of KDPG represents the outcome of an experiment conducted in natural sunlight. The parameter is a temporally averaged (e.g., over whole days, seasons, etc.) first-order photolytic transformation rate constant pertaining to cloudless conditions at some reference latitude RFLATG.
Units: /hour
Subroutines: FIRORD, PHOTO1, PRCHEM

KDTIME in labeled common TIMEL (I,S)
Internal flag indicating appropriate temporal reporting units (hours, days, months, or years).
Subroutines: DRIVER, FLXOUT, GHOST, SUMUP

KNHG(3,5) in labeled common HYDROG (R,M)
Rate constants for neutral hydrolysis of organic chemical. If the corresponding entry in the Arrhenius activation energy matrix (ENHG) for this reaction is zero, the value entered in KNHG is taken as the rate constant. If the corresponding entry in the activation energy matrix (ENHG) is non-zero, the value entered in matrix KNHG is interpreted as the base-10 logarithm of the frequency factor in an Arrhenius function for the reaction, and local values of the rate constant are computed as a function of temperature (TCELG) in each system compartment. The matrix indices for each of the 15 possible chemical species/physical form configurations of the molecule are given in the text describing matrix EAHG.
Units: /hour
Subroutines: FIRORD, PRCHEM

KO2G(NPX) in labeled common QUALG (R,V)
Reaeration parameter at 20 degrees C. in each ecosystem compartment.
Units: centimeter/hour
Subroutines: FIRORD, PRENV, VOLAT

KO2L(NPX) in labeled common FLOWSL (R,V)
Reaeration parameters in each compartment (m/hr) after temperature adjustment and units conversion.
Subroutines: FIRORD, VOLAT

KOCG in labeled common PARTG (R,S)
Multiplication of KOCG by the fractional organic carbon content (FROCG(J)) of each system sediment yields the partition coefficient for sorption of unionized (SH2) compound to the sediment.
Units: ((mg/kg)/(mg/L))/fraction organic carbon
Subroutines: DISTRB, PRCHEM

KOCL in labeled common PART1L (R,S)
Computed (or transferred from KOCG) value of KOC (c.f. KOCG). If KOCG is zero, but KOWG is non-zero, KOCL is computed from KOWG.
Subroutines: DISTRB

KOUNT in labeled common SETUPG (input variable) (I,S)
Number of compartments used to define current ecosystem.
Units: dimensionless integer
Subroutines: AVEOUT, CKLOAD, DISPER, DISTRB, DRIVER, FCT, FDER, FIRORD, FLOWS, FLXOUT, GHOST, OUTP, PRENV, PRFLOW, SEDADV, STEADY, WATADV

KOUNTS in labeled common SETUPL (R,S)
Internal count of number of sediment compartments in current ecosystem.
Subroutines: AVEOUT, DISTRB, OUTP

KOUNTW in labeled common SETUPL (R,S)
Internal count of number of water column compartments used in current ecosystem definition.
Subroutines: AVEOUT, DISTRB, OUTP

KOWG in labeled common PARTG (R,S)
Octanol-water partition coefficient of chemical. Used to compute carbon-normalized partition coefficients of neutral species (SH2) when neither Koc nor Kp have been entered in chemical data base.
Units: (mg/L)/(mg/L)
Subroutines: DISTRB, PRCHEM

KOXG(3,5) in labeled common OXIDG (R,M)
Second-order rate constants for oxidative transformations. If the corresponding entry in the Arrhenius activation energy matrix (EOXG) for this reaction is zero, the value entered in KOXG is taken as the second-order rate constant. If the corresponding entry in the activation energy matrix (EOXG) is non-zero, the value entered in matrix KOXG is interpreted as the base-10 logarithm of the frequency factor in an Arrhenius function for the reaction, and local values of the second-order rate constant are computed as a function of temperature (TCELG) in each system compartment. The matrix indices for each of the 15 possible chemical species/physical form configurations of the molecule are given in the text describing matrix EAHG.
Units: /(mole environmental oxidants/Liter) /hour
Subroutines: FIRORD, PRCHEM

KPBG(5) in labeled common PARTG (R,V)
Partition coefficient for computing sorption of chemical with compartment biomass (BIOMSG). The chemical species signified by each of the values entered in the vector is defined in the text for parameter ESOLG.
Units: (ug/gram)/(mg/Liter)
Subroutines: DISTRB, PRCHEM

KPSG(5) in labeled common PARTG (R,V)
Partition coefficients for computing sorption of chemical on compartment sediments. The chemical species signified by each of the values entered in the vector is defined in the text for parameter ESOLG. Also see KPSL.
Units: (mg/kg)/(mg/Liter)

Subroutines: DISTRB, PRCHEM

KPSL(5,NPX) in labeled common PARTIL (R,M)
Local computed values of sediment partition coefficients defining sorption of chemical to system sediments. In computing the KPSL, the input data are treated in an hierarchical fashion. Parameters that describe a dependence of KPS on properties of the environment take first precedence. Specifically, a non-zero KOCL (correlation of KPS with organic carbon content of sediments) is used to compute KPSL for the neutral species (SH2) of the molecule, giving KPSL(1,J) for the Jth compartment. If a zero value for KOCG is entered in the input data, but KOWG is non-zero, then KOCL is computed from KOWG and KOCL is used to generate KPSL(1,J). Only if KOCG and KOWG are both zero is the explicit partition coefficient for the neutral molecule (KPSG(1), which can be zero) utilized for direct computation of KPSL(1,J).

Similarly, a non-zero KCEC (correlation of KPS to cation exchange capacity of sediments) is preferentially used to compute sorption of cations to system sediments. (KCECG(1), for the singly charged cation SH3+, generates KPSL(2,J); KCECG(2), for the doubly charged cation SH4++, generates KPSL(3,J).) A non-zero KAEC is preferentially used to compute sorption of anionic species of the chemical. (KAECG(1), for the singly charged anion SH-, generates KPSL(4,J); KAECG(2), for the doubly charged anion S=, generates KPSL(5,J).) Only when KCEC or KAEC values are zero is the explicit value of the partition coefficient (KPSG) used to generate KPSL(*,J) for the ionic species of the chemical.

When KPSG values are used directly, KPSG(1) pertains to the neutral (SH2) molecule, KPSG(2) to SH3+, KPSG(3) to SH4++, KPSG(4) to SH-, and KPSG(5) to S=.
Subroutines: CKLOAD, DISTRB

KVOG in labeled common VOLATG (R,S)
Measured experimental value for (volatilization) liquid-phase transport resistance, expressed as a ratio to the reaeration rate.
Units: dimensionless ratio
Subroutines: PRCHEM, VOLAT

L in labeled common SETUPL (I,S)
Letter code for detecting (L)ittoral compartments.
Subroutines: BLOCK DATA, DISTRB, GHOST

LAMAXG in labeled common DPHOTG (R,S)
Wavelength used to calculate single-valued zenith light

extinction coefficient (CMPETG) for use in subroutine PHOTO1. LAMAXG is only used when CMPETG(J) is zero, i.e., at the user's option (Section 2.3.3.2.2).
Units: nm
Subroutines: PRCHEM, PRENV

LATG in labeled common CLIMG (R,S)
Geographic latitude of ecosystem.
Units: degrees and tenths (e.g., 37.24)
Subroutines: PHOTO1, PRENV

LIGHTL(NPX) in labeled common ENPARL (R,V)
In subroutine PHOTO1, LIGHTL(J) is computed as the average light intensity in the current (J) compartment, as a fraction of the near-surface light intensity (taken as 1.0 or 100%). In subroutine PHOTO2, LIGHTL(J) is computed as the average total irradiance in the current (J) compartment, as a fraction (%) of the total irradiance at the water surface, for that region of the solar spectrum within which the chemical absorbs light.
Subroutines: FIRORD, PHOTO1, PHOTO2

MAXPT(10) in labeled common RESLT (I,V)
Stores compartment number where the corresponding DOMAX was found.
Subroutines: AVEOUT

MINPT(10) in labeled common RESLT (I,V)
Stores compartment number where the corresponding DOMIN was found.
Subroutines: AVEOUT

MWTG in labeled common PCHEMG (R,S)
MWTG is the gram molecular weight of the chemical.
Units: grams/mole
Subroutines: CKLOAD, FIRORD, PRCHEM, VOLAT

NCON in labeled common SETUPL (I,S)
Maximum number of compartment interconnections available.
Subroutines: BLOCK DATA, DATAIN, DISPER, FLOWS, PRENV, WATADV

NPRINT in labeled common TIMEL (I,S)
Counter on calls to subroutine OUTP.
Subroutines: DRIVER

NPSCOL(NPX) in labeled common FLOWSL (R,V)
Computed concentration of sediment (kg/L) in non-point-source inputs to system compartments.
Subroutines: CKLOAD, FLOWS

NPSEDG(NPX) in labeled common FLOWG (R,V)
Non-point-source sediment loads entering ecosystem compartments.
Units: kg/hour
Subroutines: FLOWS, PRENV

NPSFL(NPX) in labeled common FLOWSL (R,V)
Local value of non-point-source water flow (L/hr) entering compartments.
Subroutines: CKLOAD, FLOWS

NPSFLG(NPX) in labeled common FLOWG (R,V)
Non-point-source water flow entering ecosystem compartments.
Units: cubic meters/hour
Subroutines: FLOWS, PRENV

NPSLDG(NPX) in labeled common LOADSG (R,V)
Chemical loadings entering compartments via non-point sources.
Units: kg/hour
Subroutines: CKLOAD, STEADY

NPX in labeled common SETUPL (I,S)
Maximum number of ecosystem compartments available.
Subroutines: BLOCK DATA, DATAIN, DISTRB, GHOST

OXIDKL(NPX) in labeled common CHEMIL (R,V)
Pseudo-first-order rate constants (/hr) for oxidative transformation of chemical in each compartment.
Subroutines: FIRORD, FLXOUT

OXRADG(NPX) in labeled common QUALG (R,V)
Molar concentration of environmental oxidants (e.g., peroxy radicals, singlet oxygen) in each ecosystem compartment.
Units: moles/Liter
Subroutines: FIRORD

PCPLDG(NPX) in labeled common LOADSG (R,V)
Chemical loadings entering each compartment via rainfall.
Units: kg/hour
Subroutines: CKLOAD, STEADY

PCTWAG(NPX) in labeled common SEDMG (R,V)
Percent water in bottom sediments of benthic compartments. Elements of this vector that correspond to water column compartments are not used (dummy values). PCTWAG should be expressed as the conventional soil-science variable (100.*fresh/dry weight); all values must be be .GE. 100. An entry in PCTWAG that is less than 100.0 for a benthic compartment raises an error condition, and program control is returned to the user for correction of the input data.
Units: dimensionless
Subroutines: DISTRB, PRENV

PHG(NPX) in labeled common QUALG (R,V)
The negative value of the power to which 10 is raised in order to obtain the temporally averaged concentration of hydronium ions $[H_3O^+]$ in gram-molecules per liter ($-\log[H^+]$).
Units: pH units
Subroutines: CKLOAD, DISTRB, FIRORD

PHOTKL(NPX) in labeled common CHEM1L (R,V)
Pseudo-first-order rate constant (/hr) for photolytic transformation of the chemical in each ecosystem compartment.
Subroutines: FIRORD, FLXOUT

PIGETA(39) in labeled common DPHOTL (R,V)
Spectral light absorption coefficients (/m/(mg/L)) for chlorophyll and chlorophyll-like pigments. Values and data sources in Section 2.3.
Subroutines: BLOCK DATA, PHOTO2, PRENV

PKAG(2) in labeled common IONG (R,V)
Negative base-10 logarithm of first and second acid dissociation constants of organic chemical. If the corresponding values of EPKAG are nonzero, however, the acidity constants are computed directly:

$$\log Ka = PKAG - (1000. * EPKAG / (2.303 * R * (TCELG + 273.15)))$$

PKAG(1) refers to generation of SH^- from SH_2; PKAG(2) refers to generation of $S^=$ from SH^-.
Subroutines: DISTRB, PRCHEM

PKBG(2) in labeled common IONG (R,V)
Negative base-10 logarithm of first and second base dissociation constants of organic chemical. If the corresponding values of EPKBG are non-zero, however, the basicity constants are computed from:

log Kb = PKBG - (1000. * EPKBG / (2.303 * R * (TCELG + 273.15)))

PKBG(1) refers to generation of SH3+ from SH2; PKBG(2) refers to generation of SH4++ from SH3+.
Subroutines: DISTRB, PRCHEM

PLRAG(NPX) in labeled common QUALG (R,V)
Fraction of total biomass (BIOMSG, c.f.) in each compartment that is planktonic, i.e., subject to passive transport via entrainment.
Units: dimensionless
Subroutines: FIRORD, PRENV

POHG(NPX) in labeled common QUALG (R,V)
The negative value of the power to which 10 is raised in order to obtain the temporally averaged concentration of hydroxide [OH-] ions in gram-molecules per liter (-log[OH-]).
Units: pOH units
Subroutines: CKLOAD, DISTRB, FIRORD

QSSAV in labeled common RESULT (R,S)
Total mass of chemical (kg) resident in benthic sediments of ecosystem at steady-state.
Subroutines: GHOST, SUMUP

QTBASG(3,5) in labeled common BACTG (R,M)
Q-10 values for bacterial transformation (c.f. KBACSG) of organic chemical in benthic sediments. The Q-10 is the increase in the second-order rate constant resulting from a 10 degree C temperature increase. The matrix indices for each of the 15 possible chemical species/physical form configurations of the molecule are given in the text describing matrix EAHG.
Units: dimensionless
Subroutines: FIRORD, PRCHEM

QTBAWG(3,5) in labeled common BACTG (R,M)
Q-10 values for bacterial transformation (c.f. KBACWG) of chemical in the water column of the system. Q-10 is the increase in the second-order rate constant resulting from a 10 degree C temperature increase. The matrix indices for each of the 15 possible chemical species/physical form configurations of the molecule are given in the text describing matrix EAHG.
Units: dimensionless
Subroutines: FIRORD, PRCHEM

QTSAV in labeled common RESULT (R,S)
Total mass of chemical resident in system at steady state.
Subroutines: GHOST, SUMUP

QUANTG(3,5) in labeled common DPHOTG (R,M)
Reaction quantum yield in photolytic transformation of chemical. The quantum yield is the fraction of total quanta absorbed by the chemical resulting in transformations. Separate values are provided for each molecular configuration of the chemical in order to make assumptions concerning their relative reactivities readily available to the user. The matrix indices for each of the 15 possible ionic species/sorbed form configurations of the chemical molecule are given in the text describing matrix EAHG.
Units: dimensionless
Subroutines: FIRORD, PRCHEM

QWSAV in labeled common RESULT (R,S)
Total mass of chemical resident in water column of system at steady state.
Subroutines: GHOST, SUMUP

RAINFL(NPX) in labeled common FLOWSL (R,V)
Rainfall entering each ecosystem compartment after conversion to internal units (L/hr).
Subroutines: CKLOAD, FLOWS

RAING in labeled common CLIMG (R,S)
Average rainfall in geographic area of system.
Units: millimeters/month
Subroutines: FLOWS, PRENV

RFLATG(5) in labeled common DPHOTG (R,V)
Reference latitude for corresponding direct photolysis rate constant (c.f. KDPG). See text describing parameter ESOLG for chemical species specified by the vector index of RFLATG.
Units: degrees and decimal fraction (e.g., 40.72)
Subroutines: PHOTO1, PRCHEM

SDCHRG(NPX) in labeled common SEDMG (R,V)
The interpretation given this parameter depends on the type of compartment involved. For water column compartments ((L)ittoral, (E)pilimnion, and (H)ypolimnion compartments), SDCHRG is the suspended sediment concentration. For (B)enthic sediment compartments, SDCHRG is the bulk density of the bottom sediment.
Units: Water column compartments: mg/Liter
Benthic compartments: grams/cubic centimeter

Subroutines: DISTRB, PHOTO2, PRENV

SEDCOL(NPX) in labeled common MASSL (R,V)
Sediment concentration after conversion to internal units (kg/Liter of water) in each compartment.
Subroutines: AVEOUT, DISPER, DISTRB, FIRORD, FLOWS, OUTP, SEDADV

SEDETA(39) in labeled common DPHOTL (R,V)
Spectral light absorption coefficients (/m/(mg/L) of suspended sediments. Values and data sources given in Section 2.3.3.
Subroutines: BLOCK DATA, PHOTO2, PRENV

SEDFL(NPX,NPX) in labeled common FLOWSL (R,M)
Matrix of sediment flows (kg/hr) among compartments.
Subroutines: DISPER, FIRORD, PRFLOW, SEDADV, WATADV

SEDMSL(NPX) in labeled common MASSL (R,V)
Mass of sediment (kg) resident in each compartment.
Subroutines: AVEOUT, DISTRB, FIRORD, PRFLOW

SEDOUL(NPX) in labeled common FLOWSL (R,V)
Export rate of sediment (kg/hr) from each compartment.
Subroutines: DISPER, FIRORD, PRFLOW, SEDADV, WATADV

SOLG(5) in labeled common PCHEMG (R,V)
Aqueous solubility. If the corresponding value in vector ESOLG (c.f.) is zero, SOLG(K) is interpreted as an aqueous solubility in mg/Liter. If ESOLG(K) is non-zero, SOLG(K) is used in an equation describing the molar solubility of the chemical species as a function of environmental temperature (TCELG), i.e.,

```
SOL (mg/L) =
    1000.*MWTG*10.**(SOLG-(1000.*ESOLG/(2.303*R*(TCELG+273.15))))
```

Solubilities are used (inter alia) to limit the permissible external loadings of the chemical on the system to values that generate final residual concentrations .LE. 50% of aqueous solubility (or 1.E-5M). This constraint is imposed in order to help ensure that the assumption of linear sorption isotherms is not seriously violated. The vector indices denote the following chemical species:

SOLG(1) -- solubility of neutral molecule (SH2)
SOLG(2) -- solubility of singly charged cation (SH3+)
SOLG(3) -- solubility of doubly charged cation (SH4++)
SOLG(4) -- solubility of singly charged anion (SH-)

SOLG(5) -- solubility of doubly charged anion (S=)

Units: mg/Liter
Subroutines: CKLOAD, PRCHEM, VOLAT

SPFLG(5) in labeled common CONTRG (I,V)
Vector containing flags that indicate which chemical species of a chemical actually exist and are thus to be considered by the program. The flags control the number of blocks (1-5) of chemical data to be recorded in the output file; the chemical data for species that do not exist is necessarily assumed to be non-existent.

SPFLG(1) set (=1) indicates the neutral molecule (SH2) exists
SPFLG(2) set indicates existence of SH3+
SPFLG(3) set indicates existence of SH4++
SPFLG(4) set indicates existence of SH-
SPFLG(5) set indicates existence of S=

Units: dimensionless
Subroutines: CKLOAD, DISTRB, FIRORD, PRCHEM, STEADY

STFLOG(NPX) in labeled common FLOWG (R,V)
Stream flow entering ecosystem compartments. Stream flows include base flow into head reach of river or estuary, tributaries, creeks entering a lake or pond, etc.
Units: cubic meters/hour
Subroutines: FLOWS, PRENV

STRLDG(NPX) in labeled common LOADSG (R,V)
Chemical loadings entering ecosystem compartments via stream flow.
Units: kg/hour
Subroutines: CKLOAD, STEADY

STRMFL(NPX) in labeled common FLOWSL (R,V)
Stream flows converted to internal units (L/hr).
Subroutines: CKLOAD, FLOWS

STSCOL(NPX) in labeled common FLOWSL (R,V)
Internal stream sediment concentrations (kg/L) for compartments.
Subroutines: CKLOAD, FLOWS

STSEDG(NPX) in labeled common FLOWG (R,V)
Stream-borne sediment load entering ecosystem compartments.
Units: kg/hour

Subroutines: FLOWS, PRENV

SYSLDL in labeled common MISCL (R,S)
Total chemical loading (kg/hr) on the ecosystem.
Subroutines: CKLOAD, FLXOUT, STEADY, SUMUP

SYSTYP(60) in labeled common NAME2G (input data) (I,V)
SYSTYP holds the name of the ecosystem being considered, with up to 60 characters permitted. SYSTYP is written in the headings for all data written to program output files.
Units: alphameric characters
Subroutines: AVEOUT, FIRORD, FLXOUT, GHOST,PRCHEM, PRENV

T in labeled common TIMEL (R,S)
Time (hrs) in numerical integration subroutine.
Subroutines: DRIVER

TCELG(NPX) in labeled common QUALG (R,V)
Average temperature of ecosystem compartments for use (as needed) in exponential functions describing chemistry of synthetic organic compounds. (The averaging method may use exponential functions.)
Units: degrees C.
Subroutines: CKLOAD, DISTRB, FIRORD

TFACTR in labeled common TIMEL (R,S)
Internal numerical factor for converting internal time (hours) to units written in output files (hours, days, months, or years).
Subroutines: FLXOUT, OUTP, SUMUP

TFINAL in labeled common TIMEL (R,S)
End point for numerical integration subroutine. TFINAL is estimated as 2 system half-lives in subroutine FLXOUT.
Subroutines: DRIVER, FLXOUT, SUMUP

TINCR in labeled common TIMEL (R,S)
Time increment between data output times in numerical integration subroutine. Computed in subroutine FLXOUT.
Subroutines: DRIVER, FLXOUT

TOTETA(39) in labeled common ENPARL (R,V)
Total spectral light absorption coefficients (/m) for ecosystem compartments.
Subroutines: PHOTO2

TOTKL(NPX) in labeled common CHEM1L (R,V)
Pseudo-first-order rate constants (/hr) for all loss processes combined, in each compartment.
Subroutines: FCT, FDER, FIRORD, STEADY

TOTLDL(NPX) in labeled common MISCL (R,V)
Total external chemical loading (kg/hr) on each ecosystem compartment.
Subroutines: CKLOAD, FIRORD, STEADY

TPRINT in labeled common TIMEL (R,S)
Times at which integrator writes to output files.
Subroutines: DRIVER

TYPEE(NPX) in labeled common NAME2G (input data) (I,V)
Letter codes designating compartment types used to define ecosystem. Available types: (L)ittoral, (E)pilimnion, (H)ypolimnion, and (B)enthic.
Units: dimensionless
Subroutines: AVEOUT, DISTRB, FIRORD, FLOWS, PHOTO1, PHOTO2, PRENV, PRFLOW

VAPRG in labeled common VOLATG (R,S)
Vapor pressure of compound. Used to compute Henry's law constant if the latter input datum (HENRYG) is zero, but VAPRG is non-zero. If EVPRG is non-zero, VAPRG is used in an equation describing vapor pressure (Pv) as a function of temperature (TCELG) in the ecosystem compartments, i.e.,

log Pv = VAPRG - (1000. * EVPRG / (2.303 * R * (TCELG + 273.15)))

Units: Torr
Subroutines: FIRORD, PRCHEM, VOLAT

VOLG(NPX) in labeled common GEOMT (R,V)
Total environmental volume of ecosystem compartments.
Units: cubic meters
Subroutines: DISPER, DISTRB, PRFLOW, VOLAT

VOLKL(NPX) in labeled common CHEM1L (R,V)
Pseudo-first-order rate constants (/hr) for volatilization losses from compartments.
Subroutines: FIRORD, FLXOUT

VOLPCT in labeled common RESLT (R,S)

Percent of total load exported via volatilization at steady state.
Subroutines: FLXOUT, SUMUP

WATETA(39) in labeled common DPHOTL (R,V)
Spectral light absorption coefficients for pure water (/m). Values and data sources given in Section 2.3.3.
Subroutines: BLOCK DATA, PHOTO2, PRENV

WATFL(NPX,NPX) in labeled common FLOWSL (R,M)
Internal matrix of water flows (L/hr) among system compartments.
Subroutines: DISPER, FIRORD, FLOWS, PRFLOW, SEDADV, WATADV

WATINL(NPX) in labeled common FLOWSL (R,V)
Total water inflow (L/hr) to compartments.
Subroutines: FLOWS, WATADV

WATOUL(NPX) in labeled common FLOWSL (R,V)
Total water export (L/hr) from compartments.
Subroutines: DISPER, FIRORD, PRFLOW, SEDADV, WATADV

WATVOL(NPX) in labeled common MASSL (R,V)
Volume of water (liters) in each compartment. /BR Subroutines: AVEOUT, DISPER, DISTRB, FIRORD, FLXOUT, OUTP, PRFLOW, STEADY

WAVEL(39) in labeled common ENPARL (R,V)
Average spectral irradiance in compartment.
Subroutines: PHOTO2

WINDG(NPX) in labeled common CLIMG (R,V)
Average wind velocity at a reference height of 10 centimeters above the water surface. Parameter is used to compute a piston velocity for water vapor (Liss 1973, Deep-Sea Research 20:221) in subroutine VOLAT.
Units: meters/second
Subroutines: FIRORD, PRENV, VOLAT

WLAMG(39) in labeled common PHOG (R,V)
Temporally averaged spectral irradiance (solar beam + sky light) immediately below the water surface (i.e., after accounting for reflection from the water surface). The 39 wavelength intervals are given in Table 2.18 of Section 2.3. An example of appropriate input data is given in Table 2.23 of Section 2.3.3.6 (cf. Zepp and Cline 1977). The input data (WLAMG) wavebands are

not identical with the full wavelength intervals used for averaging; the data are expanded to the full intervals in routine PHOTO2. For wavelength intervals 1 to 10 (covering 295-322.5 nm) N in the input unit is a 2.5 nm waveband. For wavelength interval 11 (center at 323.1 nm) the input data waveband is 3.75 nm. For wavelength intervals 12 to 39 (covering the spectral region from 325 nm through 850 nm), N in the input data (width of WLAMG waveband) is 10 nm.
Units: photons/(square cm)/second/(N nanometers)
Subroutines: PHOTO2, PRENV

WLAML(39) in labeled common ENPARL (R,V)
Local values of spectral irradiance after expansion to full wavelength intervals and pre-multiplication by numerical computation factors.
Subroutines: PHOTO2

XSTURG(3*NPX) in labeled common SETUPG (R,V)
Cross-sectional area to be applied to the dispersive exchange pairing given by the corresponding compartment numbers in vectors JTURBG and ITURBG (c.f.).
Units: square meters
Subroutines: DISPER, PRENV

Y(NPX) (R,V)
State variable vector passed through argument lists.
Subroutines: AVEOUT, DRIVER, FCT, FDER, FLXOUT, GHOST, OUTP, STEADY

YSATL(5,NPX) in labeled common FLOWSL (R,M)
Local values for aqueous solubility of 5 chemical species of the chemical (c.f. SOLG) in each ecosystem compartment.
Subroutines: CKLOAD, STEADY

Z(18) in labeled common RESULT (R,V)
Intermediate variable used for program outputs.

Z(1) -- average concentration (mg/L) of dissolved chemical in aqueous phase of water column.
Z(2) -- average concentration (mg/kg) of chemical sorbed with suspended sediments in water column.
Z(3) -- average concentration (mg/L) of chemical dissolved in interstitial water of bottom sediments.
Z(4) -- average concentration (mg/kg) of chemical sorbed with benthic sediments.
Z(5) -- total pollutant mass in water column of ecosystem (kg)
Z(6) -- total pollutant mass in benthic sediments of ecosystem

(kg)
Z(7) -- total concentration (mg/L in water column, mg/kg in benthic sediments).
Z(8) -- dissolved chemical concentration, mg/Liter of water
Z(9) -- concentration of sorbed chemical (mg/kg of sediment)
Z(10) -- concentration of biosorbed chemical, ug/g
Z(11) -- mass of chemical in compartment (g/square meter of AREAG)
Z(12) -- total kg mass of chemical in compartments
Z(13) -- average g/square meter in water column compartments
Z(14) -- average total concentration in water column (mg/L).
Z(15) -- average concentration biosorbed in water column (ug/g)
Z(16) -- average g/square meter in benthic compartments.
Z(17) -- average total concentration (mg/kg) in benthic compartments
Z(18) -- average chemical biosorbed in bottom sediments (ug/g).

Subroutines: AVEOUT, GHOST, FLXOUT, OUTP, SUMUP

GLOSSARY FOR LABELED COMMON UNITS

This glossary contains an alphabetical listing of all variables used in the interactive and simulation code of EXAMS for I/O operations. The glossary gives:

> The name of the variable
> Definition of the variable
> List of subroutines requiring the variable

All variables are of the INTEGER SCALAR type.

The program is supplied with the following assignments (set in BLOCK DATA):

UNIT	NUMBER
AUDOUT	01
INENVR	10
INCOMP	07
INDEF	08
INHLP	09
KINOUT	04
RPTOUT	02
SSOUT	03
TTYIN	05
TTYOUT	05 (06 for IBM's TSO)

AUDOUT - Logical unit number for writing the user's inputs when the AUDIT option is in effect.
Interactive subroutines: MAIN, INREC

INENVR - Logical unit number for reading and writing information to and from the environmental database.
Interactive subroutines: BLDCMD, ENVIRO, ERASE,. MAIN, RECALL, STORE, USROPT

INCOMP - Logical unit number for reading and writing

information to and from the chemical database.
Interactive subroutines: BLDCMD, COMPND, ERASE, MAIN, RECALL, STORE, USROPT

INDEF - Logical unit number for reading the description of variables used with the SHOW and DESCRIBE commands.
Interactive subroutines: BLDCMD, HELP

INHLP - Logical unit number for reading the text available via the HELP command.
Interactive subroutines: BLDCMD, BLDHLP, HELP

KINOUT - Logical unit number for writing results of numerical integration to kinetics plotting file.
Computational subroutines: BLOCK DATA, FLXOUT, GHOST, OUTP
Interactive subroutines: BLDCMD

RPTOUT - Logical unit number for data written to output report file.
Computational subroutines: AVEOUT, BLOCK DATA, DRIVER, FIRORD, OUTP, FLXOUT, GHOST, PRCHEM, PRENV, PRFLOW, STEADY, SUMUP
Interactive subroutines: BLDCMD, LISSTR, SHOW

SSOUT - Logical unit number for data written to plotting file containing EXAMS' steady-state chemical concentrations.
Computational subroutines: AVEOUT, BLOCK DATA, GHOST
Interactive subroutines: BLDCMD, PLOTX, PONDAT, PRODAT

TTYIN - Logical unit number for interactive input commands.
Computational subroutines: BLOCK DATA, PRCHEM, PRENV
Interactive subroutines: BLDCMD, COMPND, DESCRI, ENVIRO, ERASE, GETNUM, IFIND, INREC, NEWNAM, RECALL, STORE, TERMAL

TTYOUT - Logical unit number for output error messages and warnings, and for EXAMS' interactive responses.
Computational subroutines: BLOCK DATA, CKLOAD, DISPER, DISTRB, DRIVER, FLOWS, GHOST, PRCHEM, PRENV, SEDADV, STEADY, WATADV
Interactive subroutines: BLDCHA, BLDCMD, BLDECO, BLDHLP, BLDMOD, BLDNAM, COMPND, DATOPT, DESCRI, DESOUT, ENVIRO, ERASE, GETNUM, HEDSHO, HELP, IFIND, LISSTR, LIST, MAIN, MNLN, MODIFY, NEWNAM, PLOTX, PONDAT, PRTPRM, RECALL, RUNIT, SHOENV, SHOW, STAOPT, STORE, TERMAL, TYPOPT, USROPT, WHTCMD, ZONOPT

GLOSSARY FOR LABELED COMMON INPAR

This glossary contains an alphabetical listing of COMMON variables that are used in the interactive code of EXAMS. For each variable, the glossary gives:

> The name of the variable
> Dimension type (Scalar, Vector)
> Numerical size of dimensions
> Definition of the variable
> List of subroutines requiring the variable

All variables are of the INTEGER type.

AUDIT (Scalar) - allows an audit trail of user inputs to be recorded. When set to 0, no audit trail is produced; when set to 1, an audit trail is written to the dataset defined by FORTRAN unit AUDOUT.
Interactive subroutines: MAIN, INREC

CMDLEN (Vector (20)) - is used to store the lengths of the primary commands used by the executive. The Ith element of the vector contains the length of the Ith command.
Interactive subroutines: BLDCMD, WHTCMD

CMPNAM (Vector (210)) - stores the chemical (compound) names in successive elements, 1 character per element.
Interactive subroutines: BLDNAM, COMPND, SHOW

COMVAR (Vector (20)) - holds the number of variables in each labeled COMMON that can be modified via the CHANGE command. The relationship between the elements of COMVAR and the labeled COMMON is:

1 - NAME1G
2 - CONTRG
3 - PCHEMG
4 - IONG
5 - PARTG
6 - VOALTG
7 - DPHOTG
11 - LOADSG
12 - NAME2G
13 - SETUPG
14 - SEDMG
15 - QUALG
16 - PHOG
17 - GEOMT

8 - HYDROG
9 - OXIDG
10 - BACTG
18 - CLIMG
19 - FLOWG
20 - UNITS

Interactive subroutines: BLDMOD, MODIFY

ECOLEN (Vector (20)) - is used to store the lengths of the ecosystem names. The Ith element contains the length of Ith ecosystem name.
Interactive subroutines: BLDECO, ENVIRO, SHOENV

ECONAM (Vector (100)) - holds the ecosystem names in successive elements, 1 character per element.
Interactive subroutines: BLDECO, ENVIRO, SHOENV

HELEN (Vector (50)) - holds the lengths of the online assistance keywords. The Ith element of the vector contains the length of the Ith assistance keyword.
Interactive subroutines: BLDHLP, HELP

HELPS (Vector (300)) - holds the online assistance keywords in successive elements, one character per element.
Interactive subroutines: BLDHLP, HELP

IENV (Scalar) - holds the database record number of the currently selected ecosystem. If 1, then the "Unspecified" ecosystem has been selected.
Interactive subroutines: MAIN, ENVIRO, ERASE, RUNIT, SHOW, RECALL, USROPT

INPUT (Vector (80)) - contains the most recent input string received (subroutine INREC).
Interactive subroutines: BLDCMD, BLDECO, BLDHLP, BLDNAM, COMPND, DESCRI, ENVIRO, ERASE, GETNUM, HELP, IFIND, LIST, MATCH, MODIFY, NEWNAM, PRTPRM, RECALL, SCAN, STORE, TERMAL, WHTCMD

MINCMD (Vector (20)) - holds the lengths of strings required to make each string in the primary command set unique. The Ith element of the vector holds the minimum length of the Ith command string.
Interactive subroutines: BLDCMD, WHTCMD

MINCMP (Vector (60)) - holds the lengths of strings required to make each string in the set of chemical names unique. The Ith

element of the vector holds the minimum length of the Ith string.
Interactive subroutines: BLDNAM, COMPND

MINECO (Vector (20)) - holds the lengths of strings required to make each ecosystem name unique. The Ith element of the vector holds the minimum length of the Ith ecosystem name string.
Interactive subroutines: BLDECO, ENVIRO

MINHLP (Vector (50)) - holds the lengths of strings required to make each online assistance keyword unique. The Ith element of the vector holds the minimum length of the Ith online assistance keyword.
Interactive subroutines: BLDHLP, HELP

MODLEN (Vector (120)) - holds the lengths of the names of variables available to the CHANGE command. The Ith element of the vector contains the length of the Ith name.
Interactive subroutines: BLDMOD, DESCRI, HELP, MODIFY, PRTPRM, SHOW

MODMIN (Vector (120)) - holds the lengths of strings required to make each variable available to the CHANGE command unique. The Ith element of the vector holds the minimum length of the Ith string.
Interactive subroutine: BLDMOD, DESCRI, HELP, MODIFY, PRTPRM

MODS (Vector (500)) - holds the names of variables used by the CHANGE command in successive elements, one character per element.
Interactive subroutines: BLDMOD, DESCRI, HELP, MODIFY, PRTPRM, SHOW

NAMLEN (Vector (60)) - holds the lengths of the names of the compounds. The Ith element of the vector contains the length of the Ith string.
Interactive subroutine: BLDNAM, COMPND, SHOW

NCMDS (Scalar) - holds the number of primary commands available.
Interactive subroutines: BLDCMD, MAIN, WHTCMD

NOCOM (Scalar) - holds the number of labeled COMMON areas available to the CHANGE command.
Interactive subroutines: BLDMOD, MODIFY, PRTPRM

NOCREC (Scalar) - holds the maximum number of records available for the chemical data file. This value includes both user and system defined compounds.
Interactive subroutines: BLDCMD, ERASE, RECALL, STORE USROPT

NOECOS (Scalar) - holds the number of ecosystems available.
Interactive subroutines: BLDECO, ENVIRO

NOEREC (Scalar) - holds the maximum number of records available for the environmental data file. This value includes both user defined and "fixed" environments.
Interactive subroutines: BLDCMD, ERASE, RECALL, STORE, USROPT

NOHELP (Scalar) - holds the number of keywords available for use with the online assistance utility.
Interactive subroutines: BLDHLP, HELP

NOMOD (Scalar) - holds the number of variables available for use with the CHANGE command. Interactive subroutines: BLDMOD, DESCRI, HELP, MODIFY, PRTPRM, SHOW

NONAME -(Scalar) holds the number of "fixed" chemical datasets.
Interactive subroutines: BLDNAM, COMPND, ERASE, RECALL, SHOW, STORE, USROPT

POUND (Scalar) - holds the database record number of the currently, selected compound. If 1, then the "Unspecified" compound has been selected.
Interactive subroutines: COMPND, LISSTR, MAIN, RECALL

PRICMD - (Vector (200)) - is used to store the primary command strings in successive elements of the vector, one character per element.
Interactive subroutines: BLDCMD, WHTCMD

START (Scalar) - points to the starting position for scans of vectors that contain strings.
Interactive subroutines: BLDCMD, BLDECO, BLDHLP, BLDNAM, COMPND, DESCRI, ENVIRO, ERASE, GETNUM, HELP, IFIND, LIST, MATCH, MODIFY, NEWNAM, PRTPRM, RECALL, SCAN, STORE, TERMAL, WHTCMD

STOP (Scalar) - points to the ending position for the scans of vectors that contain strings.
Interactive subroutines: BLDCMD, BLDECO, BLDHLP, COMPND, DESCRI, ENVIRO, ERASE, GETNUM, HELP, IFIND, LIST, MATCH, MODIFY, PRTPRM, RECALL, SCAN, STORE, TERMAL, WHTCMD

TCOL (Vector (120)) - holds the number of columns of the matrix variables that can be modified via the CHANGE command. The Ith element contains the length of the Ith matrix variable. If the variable is not a matrix, then the Ith value of TCOL is set to 0.
Interactive subroutines: BLDMOD, DESOUT, MODIFY, PRTPRM

TD (Vector (120)) - holds the data type of variables that can be modified via the CHANGE command. The type codes are:

1 - COMPLEX
2 - DOUBLE PRECISION
3 - REAL
4 - INTEGER
5 - LOGICAL

The Ith element of the vector contains the designation for the Ith CHANGEable variable.
Interactive subroutines: BLDMOD, DESCRI, DESOUT, HELP, MODIFY, PRTPRM

TERMTY (Scalar) - holds the type of terminal in use. At present only TTY is supported.

TERMTY VALUE	TERMINAL TYPE
1	DEC VT55
2	Tektronix 4010 series
3	TTY compatible

Interactive subroutines: MAIN, INREC, TERMAL

TROW (VECTOR (120)) - holds the number of rows in a matrix, or the length of a vector, of variables that can be modified via the CHANGE command. If the variable is a scalar, TROW(I) = 0. The Ith element of the vector contains the vector length or matrix row size of the Ith CHANGEable variable.
Interactive subroutines:BLDMOD, DESOUT, MODIFY, PRTPRM

TS (VECTOR (120)) - holds the storage type of variables that can be modified via the CHANGE command. The storage codes are:

1 - Scalar
2 - Vector
3 - Matrix

The Ith element of the vector contains the code for the Ith element of CHANGEable variables.
Interactive subroutines:BLDMOD, DESOUT, MODIFY, PRTPRM

TYPE (Scalar) - holds a code denoting the delimiter that was encountered by the SCAN subroutine.
Interactive subroutines: BLDCMD, BLDECO, BLDHLP, BLDNAM, COMPND, DESCRI, ENVIRO, ERASE, GETNUM, HELP, IFIND, LIST, MODIFY, NEWNAM, PRTPRM, RECALL, SCAN, STORE, TERMAL, WHTCMD

APPENDIX A

DOCUMENTATION OF COMPUTATIONAL SUBROUTINES

EXAMS' computational subroutines are executed in the following order.

GHOST. GHOST is primarily a program control module. It performs few computations aside from preserving intermediate variables and initializing run-control parameters. GHOST opens the files for program output, writes information to the files for identifying the run, calls subroutines, and checks for error flags that may be set by the subroutines.

PRCHEM. PRCHEM records the chemical characterization of the synthetic organic (input data) in the output file defined by FORTRAN unit RPTOUT.

PRENV. PRENV records the canonical characterization of the ecosystem (input data) in the output file defined by FORTRAN unit RPTOUT.

DISTRB. DISTRB partitions the chemical among its ionic species (up to 5), with each of the ionic species further partitioned into dissolved, sediment sorbed, and biosorbed forms. The resulting distribution coefficients are used as multipliers on the (input) homogeneous-phase reaction coefficients.

FLOWS. FLOWS computes the advective and dispersive transport field that moves the chemical through the ecosystem compartments. After conversion of the input hydrologic data to a form suitable for further computations, FLOWS calls four subsidiary routines: WATADV, SEDADV, DISPER, and PRFLOW.

> WATADV. WATADV uses Gaussian elimination to calculate the total advection of water among system compartments and the magnitude of net advective exports.
>
> SEDADV. SEDADV uses the outcome of WATADV to compute chemical transport due to movement of suspended sediments, sediment exports, and bedloads.
>
> DISPER. DISPER evaluates the turbulent transport field (including boundary conditions) for water and sediments, and

generates the total chemical transport field as a sum of advective and turbulent motions.

PRFLOW. PRFLOW writes a profile of the transport characteristics of the ecosystem to the output file defined by FORTRAN unit RPTOUT.

CKLOAD. Subroutine CKLOAD accumulates the total loadings to system elements, checks to ensure that none of the loadings (via rainfall, interflow, point (stream) or non-point sources) are at aqueous concentrations (after accounting for partitioning in the input flows) greater the 50% of the aqueous solubility at the temperature specified for the system element loaded by the flow. (This constraint is imposed to maintain the linear sorption isotherms used in the model within their proper range and to prevent loadings of condensed-phase chemical.)

FIRORD. FIRORD reduces the kinetics of the chemical to pseudo-first-order form by coupling characteristics of the chemical and the environment. If the input data permit, the properties of the chemical are adjusted to reflect the effect of temperature in each physical element of the system. The pseudo-first-order reaction rate constants are computed from the interactive effects of partitioning, temperature, and other characteristics of the environment for each species or form. FIRORD also converts the input loadings and advective and dispersive flow field to pseudo-first-order effects on chemical concentrations, and writes both a kinetic profile of the chemical and a canonical profile of the ecosystem to the output data set defined by FORTRAN unit RPTOUT. FIRORD calls three subroutines (PHOTO1, PHOTO2, and VOLAT) that evaluate photolysis and volatility. (PHOTO1 and PHOTO2 are mutually exclusive computations; FIRORD selects the appropriate routine based on the structure of the input data.)

PHOTO1. PHOTO1 accepts a measured (clear day) photolysis rate constant at a specified reference latitude as input data. PHOTO1 corrects this rate constant for deviation of the latitude of the ecosystem from the reference latitude, effects of cloud cover, and light extinction in the water column based on a single-valued zenith light extinction coefficient entered as part of the canonical environmental data.

PHOTO2. PHOTO2 computes the photolysis rate constant by coupling the absorption spectrum of the chemical to the ambient light field. Light intensity in the water column is computed by assembling a total light absorption coefficient from the input data (DOC, chlorophyll, suspended sediment concentrations) and coupling this information to an input-specified near-surface spectral irradiance and distribution coefficient.

VOLAT. VOLAT computes volatilization rate constants using a two-resistance model of movement of chemical across the air-water interface.

STEADY. STEADY computes the steady-state concentrations of chemical in all system elements (using either Gaussian elimination, or, should this fail, an iterative first-order cascade technique) including the effects of internal transports among compartments.

If solubility criteria are violated as a result of drift loadings, these loads are reduced and the computations are re-evaluated. STEADY then writes a final profile of the loads to the output data set defined by FORTRAN unit RPTOUT.

AVEOUT. AVEOUT computes and reports the average, maximum, and minimum steady-state concentrations of chemical. AVEOUT also gives an element by element listing of the concentrations and distribution of chemicals throughout the ecosystem. AVEOUT writes to the output data sets defined by FORTRAN units RPTOUT and SSOUT; the latter are used for plotting the results of EXAMS' steady-state computations.

FLXOUT. FLXOUT analyzes and reports the steady-state fate of the chemical. The information reported for each process includes the mass flux (kg/time) attributable to the process, the percentage of load consumed in the process, and a projected half-life that would result from each process acting in isolation. The processes are also summed by category (chemical, biological, transport), and a total system half-life is estimated from the total flux in order to specify a time-frame for the integration routine ("DRIVER").

DRIVER. DRIVER is a dispatching and error checking routine that calls the Runge-Kutta or Gear's method (the latter is invoked for stiff equations) integration routines (RKFINT, STFINT, et seq.). The integration is carried out over two (estimated) half-lives, using the steady-state concentrations as initial conditions, in order to evaluate persistence of the chemical after the external loadings cease. The time-course of disappearance of the compound is summarized in the output data set defined by FORTRAN unit RPTOUT, and a detailed compartment-by-compartment time trace is written to the ouput data set defined by FORTRAN unit KINOUT.

SUMUP. SUMUP writes a single-page summary of the prior analyses to the output data set defined by FORTRAN unit RPTOUT, along with an estimate of the ecosystem's self-cleansing time derived from an analysis of the chemical dissipation results computed by DRIVER.

Each of EXAMS' computational subroutines is described in a separate section of this appendix. The format used for these descriptions includes the purpose of the routine, restrictions on its use, normal usage, and, where appropriate, a brief description of the algorithm or method used in the routine.

I. IDENTIFICATION

A. TITLE: DATAIN

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Jan. 1981

II. PURPOSE: DATAIN serves as a root segment for the batch version of EXAMS. Routine DATAIN pre-zeros the variables and acquires run parameters, input chemical data, and input environmental data from the appropriate files.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: GHOST

C. COMMON STORAGE:

ABSG(39,5) in labeled common DPHOTG
ACBACG(NPX) in labeled common QUALG
ADVPRG(NCON) in labeled common SETUPG
AECG(NPX) in labeled common SEDMG
AREAG(NPX) in labeled common GEOMT
BACTOG(NPX) in labeled common QUALG
BIOMSG(NPX) in labeled common QUALG
BIOTMG(NPX) in labeled common QUALG
CECG(NPX) in labeled common SEDMG
CHARLG(NCON) in labeled common SETUPG
CHEMNA(60) in labeled common NAME1G
CHLG(NPX) in labeled common PHOG
CLOUDG in labeled common PHOG
CMPETG(NPX) in labeled common PHOG
DEPTHG(NPX) in labeled common GEOMT
DFACG(NPX) in labeled common PHOG

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DOCG(NPX) in labeled common PHOG
DRFLDG(NPX) in labeled common LOADSG
DSPG(NCON) in labeled common SETUPG
EAHG(3,5) in labeled common HYDROG
EBHG(3,5) in labeled common HYDROG
EHENG in labeled common VOLATG
ENHG(3,5) in labeled common HYDROG
EOXG(3,5) in labeled common OXIDG
EPKAG(2) in labeled common IONG
EPKBG(2) in labeled common IONG
ESOLG(5) in labeled common PCHEMG
EVAPG(NPX) in labeled common CLIMG
EVPRG in labeled common VOLATG
FROCG(NPX) in labeled common SEDMG
HENRYG in labeled common VOLATG
IFLLDG(NPX) in labeled common LOADSG
INTFLG(NPX) in labeled common FLOWG
ITOADG(NCON) in labeled common SETUPG
ITURBG(NCON) in labeled common SETUPG
JFRADG(NCON) in labeled common SETUPG
JTURBG(NCON) in labeled common SETUPG
KAECG(2) in labeled common PARTG
KAHG(3,5) in labeled common HYDROG
KBACSG(3,5) in labeled common BACTG
KBACWG(3,5) in labeled common BACTG
KBHG(3,5) in labeled common HYDROG
KCECG(2) in labeled common PARTG
KDPG(5) in labeled common DPHOTG
KNHG(3,5) in labeled common HYDROG
KO2G(NPX) in labeled common QUALG
KOCG in labeled common PARTG
KOUNT in labeled common SETUPG
KOWG in labeled common PARTG
KOXG(3,5) in labeled common OXIDG
KPBG(5) in labeled common PARTG
KPSG(5) in labeled common PARTG
KVOG in labeled common VOLATG
LAMAXG in labeled common DPHOTG
LATG in labeled common CLIMG
MWTG in labeled common PCHEMG
NCON in labeled common SETUP2
NPSEDG(NPX) in labeled common FLOWG
NPSFLG(NPX) in labeled common FLOWG
NPSLDG(NPX) in labeled common LOADSG
NPX in labeled common SETUP2
OXRADG(NPX) in labeled common QUALG
PCPLDG(NPX) in labeled common LOADSG
PCTWAG(NPX) in labeled common SEDMG
PHG(NPX) in labeled common QUALG
PKAG(2) in labeled common IONG
PKBG(2) in labeled common IONG
PLRAG(NPX) in labeled common QUALG
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POHG(NPX) in labeled common QUALG
QTBASG(3,5) in labeled common BACTG
QTBAWG(3,5) in labeled common BACTG
QUANTG(3,5) in labeled common DPHOTG
RAING in labeled common CLIMG
RFLATG(5) in labeled common DPHOTG
SDCHRG(NPX) in labeled common SEDMG
SOLG(5) in labeled common PCHEMG
SPFLG(5) in labeled common CONTRG
STFLOG(NPX) in labeled common FLOWG
STRLDG(NPX) in labeled common LOADSG
STSEDG(NPX) in labeled common FLOWG
SYSTYP(60) in labeled common NAME2G
TCELG(NPX) in labeled common QUALG
TTYOUT in labeled common UNITS
TYPEE(NPX) in labeled common NAME2G
VAPRG in labeled common VOLATG
VOLG(NPX) in labeled common GEOMT
WINDG(NPX) in labeled common CLIMG
WLAMG(39) in labeled common PHOG
XSTURG(NCON) in labeled common SETUPG

IV. USAGE

A. ENTRY POINT: DATAIN

B. CALLING SEQUENCE: None

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: If the requested chemical or environmental data cannot be found, the run is aborted.

V. ALGORITHM OR METHOD -- not applicable

I. IDENTIFICATION

A. TITLE: BLOCK DATA

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Oct. 1980

II. PURPOSE: BLOCK DATA is used to load constant input data.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

B in labeled common SETUPL
BATCH in labeled common SETUPG
DOCETA(39) in labeled common DPHOTL
E in labeled common SETUPL
H in labeled common SETUPL
KINOUT in labeled common UNITS
L in labeled commmon SETUPL
NCON in labeled common SETUPL
NPX in labeled common SETUPL
PIGETA(39) in labeled common DPHOTL
RPTOUT in labeled common UNITS
SEDETA(39) in labeled common DPHOTL
SSOUT in labeled common UNITS
TTYIN in labeled common UNITS
TTYOUT in labeled common UNITS
WATETA(39) in labeled common DPHOTL

IV. USAGE

A. ENTRY POINT: None

B. CALLING SEQUENCE: None

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD -- not applicable

I. IDENTIFICATION

A. TITLE: GHOST

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Jan. 1981

II. PURPOSE: GHOST is a program control module that dimensions the state variable(s) (Y), sets error criteria, calls subroutines, preserves intermediate variables, and checks for error flags (IFLAG) that may be set by its subroutines.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED:
AVEOUT
CKLOAD
DISTRB
DRIVER
FIRORD
FLOWS
FLXOUT
PRCHEM
PRENV
STEADY
SUMUP

C. COMMON STORAGE:

CHEMNA(60) in labeled common NAME1G
ICALL in labeled common SETUPL
IFLAG in labeled common TIMEL
JSAV1 in labeled common SETUPL
JSAV2 in labeled common SETUPL
KINOUT in labeled common UNITS
KOUNT in labeled common SETUPG
NPX in labeled common SETUPL
QSSAV in labeled common RESULT
QTSAV in labeled common RESULT
QWSAV in labeled common RESULT
RPTOUT in labeled common UNITS
SSOUT in labeled common UNITS
SYSTYP(60) in labeled common NAME2G
TTYOUT in labeled common UNITS
Z(18) in labeled common RESULT

IV. USAGE

A. ENTRY POINT: GHOST

B. CALLING SEQUENCE: CALL GHOST

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS:

Returns to calling program if the number of ecosystem compartments requested by the user exceeds the maximum number available (NPX), or if any subroutine returns with IFLAG .GE. 8.

V. ALGORITHM OR METHOD -- not applicable

I. IDENTIFICATION

A. TITLE: PRCHEM

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Jan. 1981

II. PURPOSE: PRCHEM records input chemical data in an output file.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: INREC

C. COMMON STORAGE:

ABSG(39,5) in labeled common DPHOTG

BATCH in labeled common SETUPG
CHEMNA(60) in labeled common NAME1G
EAHG(3,5) in labeled common HYDROG
EBHG(3,5) in labeled common HYDROG
EHENG in labeled common VOLATG
ENHG(3,5) in labeled common HYDROG
EOXG(3,5) in labeled common OXIDG
EPKAG(2) in labeled common IONG
EPKBG(2) in labeled common IONG
ESOLG(5) in labeled common PCHEMG
EVPRG in labeled common VOLATG
HENRYG in labeled common VOLATG
KAECG(2) in labeled common PARTG
KAHG(3,5) in labeled common HYDROG
KBACSG(3,5) in labeled common BACTG
KBACWG(3,5) in labeled common BACTG
KBHG(3,5) in labeled common HYDROG
KCECG(2) in labeled common PARTG
KDPG(5) in labeled common DPHOTG
KNHG(3,5) in labeled common HYDROG
KOCG in labeled common PARTG
KOWG in labeled common PARTG
KOXG(3,5) in labeled common OXIDG
KPBG(5) in labeled common PARTG
KPSG(5) in labeled common PARTG
KVOG in labeled common VOLATG
LAMAXG in labeled common DPHOTG
MWTG in labeled common PCHEMG
PKAG(2) in labeled common IONG
PKBG(2) in labeled common IONG
QTBASG(3,5) in labeled common BACTG
QTBAWG(3,5) in labeled common BACTG
QUANTG(3,5) in labeled common DPHOTG
RFLATG(5) in labeled common DPHOTG
RPTOUT in labeled common UNITS
SOLG(5) in labeled common PCHEMG
SPFLG(5) in labeled common CONTRG
SYSTYP(60) in labeled common NAME2G
TTYIN in labeled common UNITS
TTYOUT in labeled common UNITS
VAPRG in labeled common VOLATG

IV. USAGE

A. ENTRY POINT: PRCHEM

B. CALLING SEQUENCE: CALL PRCHEM

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS:

Returns to calling program with IFLAG set to 8 if SPFLG(1) .EQ. 1 .AND. MWTG.LE.0.

V. ALGORITHM OR METHOD

Subroutine PRCHEM records the chemical characterization of the compound (input data) in the output file defined by FORTRAN logical unit RPTOUT.

I. IDENTIFICATION

A. TITLE: PRENV

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Nov. 1980

II. PURPOSE: PRENV records input environmental data in an output file and executes several data evaluation and augmentation sequences.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: INREC

C. COMMON STORAGE:

ACBACG(NPX) in labeled common QUALG
ADVPRG(NCON) in labeled common SETUPG
AECG(NPX) in labeled common SEDMG
AREAG(NPX) in labeled common GEOMT
B in labeled common SETUPL
BACTOG(NPX) in labeled common QUALG
BATCH in labeled common SETUPG
BIOMSG(NPX) in labeled common QUALG

BIOTMG(NPX) in labeled common QUALG
CECG(NPX) in labeled common SEDMG
CHARLG(NCON) in labeled common SETUPG
CHEMNA(60) in labeled common NAME1G
CHLG(NPX) in labeled common PHOG
CLOUDG in labeled common PHOG
CMPETG(NPX) in labeled common PHOG
DEPTHG(NPX) in labeled common GEOMT
DFACG(NPX) in labeled common PHOG
DOCETA(39) in labeled common DPHOTL
DOCG(NPX) in labeled common PHOG
DSPG(NCON) in labeled common SETUPG
EVAPG(NPX) in labeled common CLIMG
FROCG(NPX) in labeled common SEDMG
IFLAG in labeled common TIMEL
INTFLG(NPX) in labeled common FLOWG
ITOADG(NCON) in labeled common SETUPG
ITURBG(NCON) in labeled common SETUPG
JFRADG(NCON) in labeled common SETUPG
JTURBG(NCON) in labeled common SETUPG
KO2G(NPX) in labeled common QUALG
KOUNT in labeled common SETUPG
LAMAXG in labeled common DPHOTG
LATG in labeled common CLIMG
NCON in labeled common SETUPL
NPSEDG(NPX) in labeled common FLOWG
NPSFLG(NPX) in labeled common FLOWG
PCTWAG(NPX) in labeled common SEDMG
PIGETA(39) in labeled common DPHOTL
PLRAG(NPX) in labeled common QUALG
RAING in labeled common CLIMG
RPTOUT in labeled common UNITS
SDCHRG(NPX) in labeled common SEDMG
SEDETA(39) in labeled common DPHOTL
STFLOG(NPX) in labeled common FLOWG
STSEDG(NPX) in labeled common FLOWG
SYSTYP(60) in labeled common NAME2G
TTYIN in labeled common UNITS
TTYOUT in labeled common UNITS
TYPEE(NPX) in labeled common NAME2G
WATETA(39) in labeled common DPHOTL
WINDG(NPX) in labeled common CLIMG
WLAMG(39) in labeled common PHOG
XSTURG(NCON) in labeled common SETUPG

IV. USAGE

A. ENTRY POINT: PRENV

B. CALLING SEQUENCE: CALL PRENV

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS:

Returns to calling program with IFLAG set to 8 if the water content (PCTWAG) or bulk density (SDCHRG) of any benthic segment is zero.

V. ALGORITHM OR METHOD

Subroutine PRENV records the characteristics of the environment (input data) in the output file defined by FORTRAN logical unit RPTOUT. Several data evaluation and augmentation sequences are also executed by this subroutine:

1. Absolute zeros for FROCG, CECG, AND AECG are replaced with reasonable lower bounds (0.001, 0.01, and 0.01 respectively).

2. Absolute zeros for suspended sediments (SDCHRG of water column segments) are replaced with a value of 0.001 mg/L.

3. If CMPETG(J) is zero, LAMAXG is used to locate the corresponding spectral light absorption coefficients and compute the needed value(s) of CMPETG.

I. IDENTIFICATION

A. TITLE: DISTRB

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: May 1980

II. PURPOSE: DISTRB calculates distribution coefficients (fraction of total concentration present as a particular molecular species) for charged and uncharged chemical species (up to 5), each in a free (dissolved), sediment-sorbed, and biosorbed form.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

AECG(NPX) in labeled common SEDMG
ALPHA(18,NPX) in labeled common PART1L
AREAG(NPX) in labeled common GEOMT
B in labeled common SETUPL
BIOMSG(NPX) in labeled common QUALG
BIOTOL(NPX) in labeled common MASSL
CECG(NPX) in labeled common SEDMG
E in labeled common SETUPL
EPKAG(2) in labeled common IONG
EPKBG(2) in labeled common IONG
FROCG(NPX) in labeled common SEDMG
H in labeled common SETUPL
IFLAG in labeled common TIMEL
INDEXS(NPX) in labeled common SETUPL
INDEXW(NPX) in labeled common SETUPL
KA1L(NPX) in labeled common CHEM2L
KA2L(NPX) in labeled common CHEM2L
KAECG(2) in labeled common PARTG
KB1L(NPX) in labeled common CHEM2L
KB2L(NPX) in labeled common CHEM2L
KCECG(2) in labeled common PARTG
KOCG in labeled common PARTG
KOCL in labeled common PART1L
KOUNT in labeled common SETUPG
KOUNTS in labeled common SETUPL
KOUNTW in labeled common SETUPL
KOWG in labeled common PARTG
KPBG(5) in labeled common PARTG
KPSG(5) in labeled common PARTG
KPSL(5,NPX) in labeled common PART1L
L in labeled common SETUPL
NPX in labeled common SETUPL
PCTWAG(NPX) in labeled common SEDMG
PHG(NPX) in labeled common QUALG
PKAG(2) in labeled common IONG
PKBG(2) in labeled common IONG
POHG(NPX) in labeled common QUALG
SEDCHRG(NPX) in labeled common SEDMG
SEDCOL(NPX) in labeled common MASSL
SEDMSL(NPX) in labeled common MASSL

SPFLG(5) in labeled common CONTRG
TCELG(NPX) in labeled common QUALG
TTYOUT in labeled common UNITS
TYPEE(NPX) in labeled common NAME2G
VOLG(NPX) in labeled common GEOMT
WATVOL(NPX) in labeled common MASSL

IV. USAGE

A. ENTRY POINT: DISTRB

B. CALLING SEQUENCE: CALL DISTRB

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS:

Returns to calling program with IFLAG set to 8 if any compartment type (TYPEE) is improper.

V. ALGORITHM OR METHOD

Subroutine DISTRB partitions the chemical among its ionic species (up to 5), with each of the ionic species further partitioned into dissolved, sediment-sorbed, and biosorbed forms. The resulting distribution coefficients (ALPHA) are subsequently (subroutine FIRORD) used as multipliers on the (input data) homogeneous-phase reaction rate coefficients. The (DISTRB) input data for ionization includes the pKa of organic acids and pKb of organic bases. These data may be loaded either as single values or as temperature functions; in the latter case the temperature (TCELG) of each compartment is used to compute a local value of the ionization constant. Sorption to biomass and to whole sediments are also treated as equilibrium processes. For biomass sorption, the equilibrium constant (partition coefficient) is loaded as a single value for each chemical species (KPBG). The partition coefficient for whole sediments can be loaded in several ways; this feature is described in the glossary for EXAMS under "KPSL" and in Section 2.2.2.

The fraction of the total concentration (Y state variable) present in each of the 15 possible molecular configurations (dissolved neutral molecule, etc.) is loaded to the ALPHA matrix. ALPHA contains as many columns as there are ecosystem segments, and also includes the total dissolved, sediment-sorbed, and biosorbed fractions (as

ALPHA 16, 17, and 18).

The chemical equations for the pK of ionic species and the partitioning coefficients of each ion, together with the conservation condition (sum of all species/forms = total concentration) give a set of 15 equations in 15 unknowns for the 15 distribution coefficients (ALPHA). The (pre-computed) solution to this system of equations is the heart of the code for subroutine DISTRB. For each ecosystem compartment, the contribution of each species/form configuration (DISFCT(I)) is computed, their sum is taken, and then each ALPHA is computed as the ratio of DISFCT(I) to that sum.

I. IDENTIFICATION

A. TITLE: FLOWS

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: May 1980

II. PURPOSE: FLOWS computes advective and dispersive transport fields for water and sediments in a steady-state aquatic ecosystem.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: DISPER
PRFLOW
SEDADV
WATADV

C. COMMON STORAGE:

AREAG(NPX) in labeled common GEOMT
B in labeled common SETUPL
EVAPG(NPX) in labeled common CLIMG
EVAPL(NPX) in labeled common FLOWSL

H in labeled common SETUPL
IFLAG in labeled common TIMEL
INDEXW(NPX) in labeled common SETUPL
INTFL(NPX) in labeled common FLOWSL
INTFLG(NPX) in labeled common FLOWG
JFRADG(NCON) in labeled common SETUPG
KOUNT in labeled common SETUPG
NCON in labeled common SETUPL
NPSCOL(NPX) in labeled common FLOWSL
NPSEDG(NPX) in labeled common FLOWG
NPSFL(NPX) in labeled common FLOWSL
NPSFLG(NPX) in labeled common FLOWG
RAINFL(NPX) in labeled common FLOWSL
RAING in labeled common CLIMG
STFLOG(NPX) in labeled common FLOWG
STRMFL(NPX) in labeled common FLOWSL
STSCOL(NPX) in labeled common FLOWSL
STSEDG(NPX) in labeled common FLOWG
TTYOUT in labeled common UNITS
TYPEE(NPX) in labeled common NAME2G
WATFL(NPX,NPX) in labeled common FLOWSL
WATINL(NPX) in labeled common FLOWSL

IV. USAGE

A. ENTRY POINT: FLOWS

B. CALLING SEQUENCE: CALL FLOWS

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS:

Returns to calling program with IFLAG set to 8 if:

1) any compartment is completely disconnected from the main body of the system, or

2) subroutine WATADV sets IFLAG to 8.

V. ALGORITHM OR METHOD

Subroutine FLOWS is primarily a dispatching routine. FLOWS converts the global (input) parameters describing the hydrology, geometry, and sediment loads in the ecosystem to their internal dimensions, computes the net advective flow in each compartment, checks for erroneous input data, and calls on four additional subroutines to compute the advective (WATADV, SEDADV) and dispersive (DISPER) transport fields, and to print the results (PRFLOW).

I. IDENTIFICATION

A. TITLE: WATADV

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Jan. 1981

II. PURPOSE: WATADV calculates the total advection of water among ecosystem compartments, and the magnitude of net advective exports.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

ADVPRG(NCON) in labeled common SETUPG
IFLAG in labeled common TIMEL
ITOADG(NCON) in labeled common SETUPG
JFRADG(NCON) in labeled common SETUPG
KOUNT in labeled common SETUPG
NCON in labeled common SETUPL
SEDFL(NPX,NPX) in labeled common FLOWSL
SEDOUL(NPX) in labeled common FLOWSL
TTYOUT in labeled common UNITS
WATFL(NPX,NPX) in labeled common FLOWSL
WATINL(NPX) in labeled common FLOWSL
WATOUL(NPX) in labeled common FLOWSL

IV. USAGE

A. ENTRY POINT: WATADV

B. CALLING SEQUENCE: CALL WATADV(TOTIN)

C. INPUT ARGUMENTS: TOTIN - total water flow entering system from all sources, less total evaporation.

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS:

Returns to calling program with IFLAG set to 8 if:

1) flows through any compartment have been defined in a way that violates mass conservation,

2) the nominal (input) water budget for the whole system fails to conserve mass, or

3) the Gaussian elimination processor fails.

V. ALGORITHM OR METHOD

The mass-conservative equations for hydrologic transport through an n-compartment system are solved by Gaussian elimination.

I. IDENTIFICATION

A. TITLE: SEDADV

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: May 1980

II. PURPOSE: SEDADV computes transport of synthetic organics via an evaluation of transport of suspended sediments among system compartments, sediment exports, and bedload sediment transport in an aquatic ecosystem.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

IFLAG in labeled common TIMEL
INDEXS(NPX) in labeled common SETUPL
KOUNT in labeled common SETUPG
SEDCOL(NPX) in labeled common MASSL
SEDFL(NPX,NPX) in labeled common FLOWSL
SEDOUL(NPX) in labeled common FLOWSL
TTYOUT in labeled common UNITS
WATFL(NPX,NPX) in labeled common FLOWSL
WATOUL(NPX) in labeled common FLOWSL

IV. USAGE

A. ENTRY POINT: SEDADV

B. CALLING SEQUENCE: CALL SEDADV

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: Returns to calling program with IFLAG=8 if compartment #1 is a bottom sediment.

V. ALGORITHM OR METHOD

Subroutine SEDADV uses the advective flow field for water (computed by subroutine WATADV) to compute the entrained transport of suspended sediments, sediment exports, and bedloads. This treatment of sediment flows of necessity assumes that the system compartments have been numbered in a logical way. Compartment #1 must be a water column. The system block diagram must then be numbered in vertical order, proceeding along the main advective flow path. For example, for a river system with two vertical sediment compartments in each reach, compartment #1 would designate the water column of the first reach, #2 the shallow sediment of the first reach, #3 its deeper sediment; #4 the water column of the second reach, #5 its shallow sediment, #6 its deeper sediment, etc.

Given this numbering scheme, advected flows among sediment compartments are permitted, so that bed-loads can move along the advective flow path(s) of the system. Advective flows from the water column into the sediments (and vice versa), however, are taken to involve a flow of contaminated water only (as in groundwater seepage or recharge).

Because either sediment genesis or degradation (remineralization) can occur within system elements, the system sediments are treated as a non-conservative constituent. Thus the sediment concentrations in the system compartments (input data loaded by the user) are used directly in the computations, and no attempt is made to construct a sediment budget from the input (stream, non-point-source) sediment loadings. The latter are simply used to constrain chemical loadings to more-or-less reasonable values (see subroutine CKLOAD).

The program provides for exchanges of sediments with external sources and sinks (i.e., boundary condition dispersive exchanges), so the total sediment budget cannot be explicitly determined.

Thus in summary, exports of water across system boundaries carry an entrained sediment flow except in the case where the outflow is from a bottom sediment compartment AND the (J-1) compartment is also a sediment. Intra-system transport of entrained sediment is subject to three constraints: First, advective flows between water columns carry a sediment load determined by the sediment concentration in the source compartment. Second, advective flows involving a sediment--water column pair are constrained to a water flow only (ground water seepage and recharge). Third, advection between sediments entrains a parallel sediment flow only when the compartment numbers indicate that the sediments are not vertically connected (i.e., the compartment numbers differ by more than one digit). (See Section 2.3.1.3.)

I. IDENTIFICATION

A. TITLE: DISPER

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Jul. 1980

II. PURPOSE: DISPER calculates a dispersive transport field (including boundary conditions) for water and sediments in an aquatic ecosystem, and generates a total transport field as the sum of advective and dispersive components.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

ALPHA(18,NPX) in labeled common PART1L
CHARLG(NCON) in labeled common SETUPG
DSPG(NCON) in labeled common SETUPG
INDEXS(NPX) in labeled common SETUPL
INDEXW(NPX) in labeled common SETUPL
ITURBG(NCON) in labeled common SETUPG
JTURBG(NCON) in labeled common SETUPG
KOUNT in labeled common SETUPG
NCON in labeled common SETUPL
SEDCOL(NPX) in labeled common MASSL
SEDFL(NPX,NPX) in labeled common FLOWSL
SEDOUL(NPX) in labeled common FLOWSL
TTYOUT in labeled common UNITS
VOLG(NPX) in labeled common GEOMT
WATFL(NPX,NPX) in labeled common FLOWSL
WATOUL(NPX) in labeled common FLOWSL
WATVOL(NPX) in labeled common MASSL
XSTURG(NCON) in labeled common SETUPG

IV. USAGE

A. ENTRY POINT: DISPER

B. CALLING SEQUENCE: CALL DISPER

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

Computation of dispersive flows: In this series of computations, the chemical transport arising from dispersive mass transport is computed from input data for dispersive compartment pairings (JTURBG and ITURBG), cross-sectional area (XSTURG, square meters), characteristic length (CHARLG, meters), and eddy diffusivity (DSPG, square meters per hour) specified for the exchange pairing. All boundary conditions for dispersive exchange across system boundaries are taken as zero in chemical concentration because, otherwise, the estimates of persistence of the chemical (after loads are removed) become intractable.

The processes occurring in the water column are rather different from those occurring within the sediments or at the sediment-water interface, even though the computational treatment is similar. The basic computation (DSPG * XSTURG / CHARLG) results in a quantity with dimensions of cubic meters per hour, and nominally refers to transport of a cubic meter of environmental volume. For transport among water column compartments this presents no difficulty -- the water flow is given directly, and (given the non-conservative treatment of sediment used in the program) the parallel sediment flows are computed from the suspended sediment concentrations in the source compartments. Chemical exchange involving bed sediments must also account for differences in the sorptive capacity of the bed layers and the washload. EXAMS' treatment of this process is discussed in Section 2.3.1.4.

I. IDENTIFICATION

A. TITLE: PRFLOW

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Jul. 1980

II. PURPOSE: PRFLOW writes a profile of the chemical transport characteristics of an aquatic ecosystem to an output file.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

KOUNT in labeled common SETUPG
RPTOUT in labeled common UNITS
SEDFL(NPX,NPX) in labeled common FLOWSL
SEDMSL(NPX) in labeled common MASSL
SEDOUL(NPX) in labeled common FLOWSL
TYPEE(NPX) in labeled common NAME2G
VOLG(NPX) in labeled common GEOMT
WATFL(NPX,NPX) in labeled common FLOWSL
WATOUL(NPX) in labeled common FLOWSL
WATVOL(NPX) in labeled common MASSL

IV. USAGE

A. ENTRY POINT: PRFLOW

B. CALLING SEQUENCE: CALL PRFLOW

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

Subroutine PRFLOW writes a compartment-by-compartment summary of chemical transport characteristics of the ecosystem to the output file defined by FORTRAN logical unit RPTOUT.

The variables reported include: compartment volumes, total sediment masses, water and sediment flows, and residence (turnover) times for water and sediments. The compartment volumes are input data (VOLG); the sediment masses are computed in subroutine FLOWS. Subroutine PRFLOW computes the total chemical movement associated with water and sediment transport through the compartments by summing the advective plus dispersive flows loaded in matrices WATFL and SEDFL and vectors WATOUL and SEDOUL (these variables are loaded by subroutine DISPER). Residence times are then computed as the ratio of water volume or sediment mass to the appropriate flow quantity. The value loaded to the SEDFL matrix via dispersive processes can vary if the sorptive capacity of the sediments differs, i.e., the computed residence times can differ as a function of properties of the chemical (see Section 2.3.1.4).

I. IDENTIFICATION

A. TITLE: CKLOAD

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Jan. 1981

II. PURPOSE

PURPOSE: CKLOAD constrains chemical loadings to values that do not exceed 50% of the aqueous solubility or 1.E-5 M (after accounting for sorption), checks that input carrier flows exist for each posited loading, and accumulates the total compartment loadings.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

DRFLDG(NPX) in labeled common LOADSG
ESOLG(5) in labeled common PCHEMG
IFLAG in labeled common TIMEL
IFLLDG(NPX) in labeled common LOADSG
INTFL(NPX) in labeled common FLOWSL
KA1L(NPX) in labeled common CHEM2L
KA2L(NPX) in labeled common CHEM2L
KB1L(NPX) in labeled common CHEM2L
KB2L(NPX) in labeled common CHEM2L
KOUNT in labeled common SETUPG
KPSL(5,NPX) in labeled common PART1L
MWTG in labeled common PCHEMG
NPSCOL(NPX) in labeled common FLOWSL

NPSFL(NPX) in labeled common FLOWSL
NPSLDG(NPX) in labeled common LOADSG
PCPLDG(NPX) in labeled common LOADSG
PHG(NPX) in labeled common QUALG
POHG(NPX) in labeled common QUALG
RAINFL(NPX) in labeled common FLOWSL
SOLG(5) in labeled common PCHEMG
SPFLG(5) in labeled common CONTRG
STRLDG(NPX) in labeled common LOADSG
STRMFL(NPX) in labeled common FLOWSL
STSCOL(NPX) in labeled common FLOWSL
SYSLDL in labeled common MISCL
TCELG(NPX) in labeled common QUALG
TOTLDL(NPX) in labeled common MISCL
TTYOUT in labeled common UNITS
YSATL(5,NPX) in labeled common FLOWSL

IV. USAGE

A. ENTRY POINT: CKLOAD

B. CALLING SEQUENCE: CALL CKLOAD

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: If no positive loadings remain, IFLAG is set to 8.

V. ALGORITHM OR METHOD

Subroutine CKLOAD accumulates the total loadings to system elements (compartments), removes loadings that lack an associated input carrier flow, and checks to ensure that none of the loadings (via rainfall, interflow (ground-water seepage), point (stream), or non-point sources are at aqueous concentrations (after accounting for partitioning to sediments in the input flows) greater than 50% of aqueous solubility at the temperature specified for the system element receiving the load, or 1.E-5 M in SH2. (This constraint is imposed to ensure that the simulation run is in accord with the intrinsic assumptions used to develop the program, e.g., that linear sorption isotherms are proper, and that the chemical loadings do not include solid particles.)

The computational scheme used in CKLOAD is, in principle, the same as that used in subroutine DISTRB, i.e., the code contains the solution to systems of linear equations describing the distribution coefficients (local variable BETA for the 5 or 10 possible molecular species). Those cases requiring water quality data (e.g., water temperature or pH) use input data for the target compartment of the loading under review. When the residual concentration exceeds the concentration limit, the load is reduced and an informative message is written to the user in the output data set defined by FORTRAN logical unit TTYOUT.

I. IDENTIFICATION

A. TITLE: FIRORD

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Nov. 1980

II. PURPOSE: FIRORD merges environmental data and chemical characteristics of an organic compound to yield a pseudo-first-order description of the chemical's kinetic behavior.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: PHOTO1
PHOTO2
VOLAT

C. COMMON STORAGE:

ABSG(39,5) in labeled common DPHOTG
ACBACG(NPX) in labeled common QUALG
ALPHA(18,NPX) in labeled common PART1L
B in labeled common SETUPL
BACTOG(NPX) in labeled common QUALG
BIOLKL(NPX) in labeled common CHEM1L
BIOTMG(NPX) in labeled common QUALG

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CHEMNA(60) in labeled common NAME1G
CONLDL(NPX) in labeled common MISCL
EAHG(3,5) in labeled common HYDROG
EBHG(3,5) in labeled common HYDROG
ENHG(3,5) in labeled common HYDROG
EOXG(3,5) in labeled common OXIDG
EXPOKL(NPX) in labeled common CHEM1L
H in labeled common SETUPL
HENRYG in labeled common VOLATG
HYDRKL(NPX) in labeled common CHEM1L
INDEXS(NPX) in labeled common SETUPL
INDEXW(NPX) in labeled common SETUPL
INTINL(NPX,NPX) in labeled common CHEM1L
KAHG(3,5) in labeled common HYDROG
KBACSG(3,5) in labeled common BACTG
KBACWG(3,5) in labled common BACTG
KBHG(3,5) in labeled common HYDROG
KDPG(5) in labeled common DPHOTG
KNHG(3,5) in labeled common HYDROG
KO2(NPX) in labeled common QUALG
KO2L(NPX) in labeled common FLOWSL
KOUNT in labeled common SETUPG
KOXG(3,5) in labeled common OXIDG
LIGHTL(NPX) in labeled common ENPARL
MWTG in labeled common PCHEMG
OXIDKL(NPX) in labeled common CHEM1L
OXRADG(NPX) in labeled common QUALG
PHG(NPX) in labeled common QUALG
PHOTKL(NPX) in labeled common CHEM1L
PLRAG(NPX) in labeled common QUALG
POHG(NPX) in labeled common QUALG
QTBASG(3,5) in labeled common BACTG
QTBAWG(3,5) in labeled common BACTG
QUANTG(3,5) in labeled common DPHOTG
RPTOUT in labeled common UNITS
SEDCOL(NPX) in labeled common MASSL
SEDFL(NPX,NPX) in labeled common FLOWSL
SEDMSL(NPX) in labeled common MASSL
SEDOUL(NPX) in labeled common FLOWSL
SPFLG(5) in labeled common CONTRG
SYSTYP(60) in labeled common NAME2G
TCELG(NPX) in labeled common QUALG
TOTKL(NPX) in labeled common CHEM1L
TOTLDL(NPX) in labeled common MISCL
TYPEE(NPX) in labeled common NAME2G
VAPRG in labeled common VOLATG
VOLKL(NPX) in labeled common CHEM1L
WATFL(NPX,NPX) in labeled common FLOWSL
WATOUL(NPX) in labeled common FLOWSL
WATVOL(NPX) in labeled common MASSL
WINDG in labeled common CLIMG
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IV. USAGE

A. ENTRY POINT: FIRORD

B. CALLING SEQUENCE: CALL FIRORD

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

[redacted]

V. ALGORITHM OR METHOD

This routine reduces system-independent process models describing the kinetics of a synthetic organic chemical to pseudo-first-order form by coupling characteristics of the chemical and of the environment. Insofar as the input data permits, the chemical properties of the compound are adjusted (via Arrhenius functions) to reflect the effect of temperature in each physical element (compartment) of the system. The pseudo-first-order reaction rate constants are calculated from the interactive effects of partitioning, temperature, and other relevant charateristics of the environment (pH, pOH, irradiance, advection, bacterial population sizes, etc.) for each ionic species/sorbed form of the chemical present; the reactivities of the several varieties are summed to give a total pseudo-first-order rate constant. The routine accounts for the potential existence of five ionic species (neutral molecule, singly and doubly charged cations and anions), each of which may occur in three sorbed forms (dissolved, sediment-sorbed, bio-sorbed.

The processes evaluated include photolysis, volatilization, hydrolysis, oxidation, bacterial biolysis, transport, and ionization and sorption equilibria. Routine FIRORD also converts the external input loadings and the advective and dispersive flow field into pseudo-first-order effects on chemical concentrations and writes both a kinetic profile of the compound and a canonical profile of the ecosystem to the file defined by FORTRAN logical unit RPTOUT. Routine FIRORD also calls three subroutines (PHOTO1, PHOTO2, and VOLAT) that evaluate photolysis and volatility. (PHOTO1 and PHOTO2 are mutually exclusive computations; FIRORD selects the appropriate routine based on the structure of the input data.)

I. IDENTIFICATION

A. TITLE: PHOTO1

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Oct. 1980

II. PURPOSE:

PHOTO1 corrects an experimental pseudo-first-order rate constant for photolytic decomposition of a synthetic organic chemical in the water column of an aquatic ecosystem for effects of cloud cover, water depth, and deviation of the latitude of the ecosystem from that of the location where the experiment was executed.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

BOTLIT in labeled common ENPARL
CLOUDG in labeled common PHOG
CMPETG(NPX) in labeled common PHOG
DEPTHG(NPX) in labeled common GEOMT
DFACG(NPX) in labeled common PHOG
E in labeled common SETUPL
H in labeled common SETUPL
JSAV1 in labeled common SETUPL
KDPG(5) in labeled common DPHOTG
LATG in labeled common CLIMG
LIGHTL(NPX) in labeled common ENPARL
RFLATG(5) in labeled common DPHOTG
TYPEE(NPX) in labeled common NAME2G

IV. USAGE

A. ENTRY POINT: PHOTO1

B. CALLING SEQUENCE: CALL PHOTO1(RATEK,K,J)

C. INPUT ARGUMENTS: K - index value for chemical species
J - index value for ecosystem compartment

D. OUTPUT ARGUMENTS: RATEK: pseudo-first-order photolysis rate constant

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

The basic unit of input to PHOTO1 is a first-order photolysis rate constant of a synthetic chemical, generated via experimental studies. This rate constant is assumed to represent a temporally averaged value applicable under cloudless conditions in near-surface waters at some reference latitude (RFLATG). Distinct values of the rate constant (KDPG(K)) and reference latitude (RFLATG(K)) may be entered for each of five possible ionic species of the chemical (neutral molecule, singly and doubly charged cations and anions). PHOTO1 applies the Beer-Lambert law to compute the reduction in rate due to light absorption in the water column of the system. Light intensity at the water surface is taken as unity, and the average (relative) light intensity in the water column is computed as a function of depth (DEPTHG(J)), a single-valued zenith light extinction coefficient (CMPETG(J)), and a distribution function (DFACG(J)) for the current (J) compartment. If the current (J) compartment has an overlying water mass, the relative intensity at the bottom of this overlying water (computed on a previous call to PHOTO1) is used as the starting point for computations in the current (J) compartment.

An additional reduction in rate is calculated to account for cloud cover, and the rate constant for the current (K) chemical species is finally adjusted for the difference in latitude between the location of the ecosystem and the experimental studies. The latitude correction is based on a cosine function describing total annual light input (solar beam + sky light) at sea level (data from Smithsonian Meteorological Tables (List 1966)).

I. IDENTIFICATION

A. TITLE: PHOTO2

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Sep. 1980

II. PURPOSE: PHOTO2 calculates the rate of light absorption by a chemical in a water column compartment of an aquatic ecosystem. The value returned by the routine can be multiplied by a reaction quantum yield to give a pseudo-first-order rate constant for photolytic decomposition of the chemical.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

ABSG(39,5) in labeled common DPHOTG
BOTLAM(39) in labeled common ENPARL
CHLG(NPX) in labeled common PHOG
CLOUDG in labeled common PHOG
DEPTHG(NPX) in labeled common GEOMT
DFACG(NPX) in labeled common PHOG
DOCETA(39) in labeled common DPHOTL
DOCG(NPX) in labeled common PHOG
E in labeled common SETUPL
H in labeled common SETUPL
ICALL in labeled common SETUPL
JSAV2 in labeled common SETUPL
LIGHTL(NPX) in labeled common ENPARL
PIGETA(39) in labeled common DPHOTL
SDCHRG(NPX) in labeled common SEDMG
SEDETA(39) in labeled common DPHOTL
TOTETA(39) in labeled common ENPARL
TYPEE(NPX) in labeled common NAME2G
WATETA(39) in labeled common DPHOTL
WAVEL(39) in labeled common ENPARL
WLAMG(39) in labeled common PHOG
WLAML(39) in labeled common ENPARL

IV. USAGE

A. ENTRY POINT: PHOTO2

B. CALLING SEQUENCE: CALL PHOTO2(RATEK,K,J)

C. INPUT ARGUMENTS: K - index value for chemical species

J - index value for ecosystem compartment

D. OUTPUT ARGUMENTS: RATEK - rate of absorption of light by synthetic organic chemical

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

This routine adjusts the near-surface spectral irradiance (WLAMG) for effects of cloud cover, fills out wavelength intervals (e.g., for interval 39, the input data has dimensions /10 nm, but the full width of the interval is 50 nm), and pre-multiplies all data by a units conversion FACTOR, with the outcome stored in WLAML. For each water column, a (spectral) total light absorption coefficient is assembled as the sum of contributions from water itself, suspended sediments (SDCHRG), dissolved organic carbon (DOCG), and chlorophyll and chlorophyll-like pigments (CHLG). The Beer-Lambert law is then used to compute light absorption and average spectral irradiance within the water column compartment. If the current (J) compartment has an overlying water-mass, spectral irradiance at the bottom of this overlying water (computed on a previous call to PHOTO2) is used as a starting point for computations in the current (J) compartment. Light absorption by the current (K) ionic species of a chemical is computed by coupling the average spectral irradiance in the water column, the absorption spectrum of the compound, and the distribution function of the current (J) compartment. The routine assumes that the chemical itself does not contribute significantly to the total light absorption coefficient. The algorithm is described in detail in Section 2.3.3.

I. IDENTIFICATION

A. TITLE: VOLAT

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Jul. 1980

II. PURPOSE: VOLAT computes a pseudo-first-order rate constant describing the export of a synthetic organic chemical across the air-water interface of an aquatic ecosystem.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

AREAG(NPX) in labeled common GEOMT
EHENG in labeled common VOLATG
ESOLG(5) in labeled common PCHEMG
EVPRG in labeled common VOLATG
HENRYG in labeled common VOLATG
KO2G(NPX) in labeled common QUALG
KO2L(NPX) in labeled common FLOWSL
KVOG in labeled common VOLATG
MWTG in labeled common PCHEMG
SOLG(5) in labeled common PCHEMG
TCELG(NPX) in labeled common QUALG
VAPRG in labeled common VOLATG
VOLG(NPX) in labeled common GEOMT
WINDG(NPX) in labeled common CLIMG

IV. USAGE

A. ENTRY POINT: VOLAT

B. CALLING SEQUENCE: CALL VOLAT(K,BETA,RATEK)

C. INPUT ARGUMENTS: K - index value for ecosystem compartment

BETA - fraction of total concentration of chemical that is present as neutral (uncharged), dissolved species.

D. OUTPUT ARGUMENTS: RATEK - pseudo-first-order rate constant for volatilization

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

VOLATG uses a two-resistance model (Whitman 1923) to compute a pseudo-first-order rate constant for volatilization losses of a synthetic organic chemical across the air-water interfaces of an aquatic ecosystem. The bulk air concentration of the chemical is assumed to be negligible. The first-order rate constant is computed as the total transport conductivity (reciprocal of the sum of resistances to transport in the liquid and gas phases) multiplied by the fraction of the total concentration of the chemical present in transportable (i.e., unsorbed, uncharged) form (input argument BETA), times the surface to volume ratio of the current (K) compartment. The routine corrects the input reaeration parameter (cm/hr at 20 degrees C.) for the temperature of the current (K) compartment. Liquid phase resistance is computed either from an experimentally determined ratio to the reaeration rate, or, if this parameter (KVOG) is entered as a zero, resistance is estimated from the square root of the ratio of molecular weights of oxygen and the chemical. Gas phase resistance is estimated from the Henry's law constant of the chemical, temperature, the molecular weight ratio of the chemical to the molecular weight of water, and a piston velicity for water vapor computed from the input values for windspeed (Liss 1973). If a zero value is loaded for the Henry's law constant, this parameter is estimated from the vapor pressure/solubility ratio.

I. IDENTIFICATION

A. TITLE: STEADY

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Jan. 1981

II. PURPOSE: STEADY computes the steady-state concentration of synthetic organic chemicals in all active ecosystem compartments.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

ALPHA(18,NPX) in labeled common PART1L
BATCH in labeled common SETUPG
CONLDL(NPX) in labeled common MISCL
DRFLDG(NPX) in labeled common LOADSG
IFLAG in labeled common TIMEL
IFLLDG(NPX) in labeled common LOADSG
INTINL(NPX,NPX) in labeled common CHEM1L
KOUNT in labeled common SETUPG
NPSLDG(NPX) in labeled common LOADSG
PCPLDG(NPX) in labeled common LOADSG
RPTOUT in labeled common UNITS
SPFLG(5) in labeled common CONTRG
STRLDG(NPX) in labeled common LOADSG
SYSLDL in labeled common MISCL
TOTKL(NPX) in labeled common CHEM1L
TOTLDL(NPX) in labeled common MISCL
TTYOUT in labeled common UNITS
WATVOL(NPX) in labeled common MASSL
YSATL(5,NPX) in labeled common FLOWSL

IV. USAGE

A. ENTRY POINT: STEADY

B. CALLING SEQUENCE: CALL STEADY(Y)

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: Y - steady-state concentration vector

E. ERROR CONDITIONS AND RETURNS:

Returns to calling program with IFLAG set to 8 if final concentrations exceed solubility criteria.

V. ALGORITHM OR METHOD

The steady-state concentration vector (Y) is computed by Gaussian elimination. The processor matrix is loaded with INTINL (transport), (-TOTKL) on the diagonal, and (normalized) zero-order loadings expressed in terms of their effect on concentration (-CONLDL). For those cases in which Gaussian elimination fails, a linear cascade technique is invoked to compute Y. In this algorithm, the algebraic solution

Y(J)= {CONLDL(J) + [sum(over I) INTINL(I,J)*Y(I)]}/TOTKL(J)

is iterated to convergence.

After computation of steady-state values, the concentration in each compartment is checked to ensure that the residual dissolved concentrations do not exceed 50% of aqueous solubility or 1.E-5 M in SH2 (to maintain simulations in accord with program assumptions). If this criterion is violated, drift loadings entering the system are reduced and the steady-state computations are repeated.

Having achieved an acceptable steady-state solution, STEADY writes a tabulation of the final loadings to the output file defined by FORTRAN logical unit RPTOUT.

I. IDENTIFICATION

A. TITLE: AVEOUT

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Jan. 1981

II. PURPOSE: AVEOUT computes and reports average, maximum, and minimum steady-state concentrations of chemical and gives an element-by-element listing of concentrations and distribution of chemical throughout the ecosystem.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

ALPHA(18,NPX) in labeled common PARTIL
AREAG(NPX) in labeled common GEOMT

BIOTOL(NPX) in labeled common MASSL
CHEMNA(60) in labeled common NAME1G
DOMAX(10) in labeled common RESLT
DOMIN(10) in labeled common RESLT
INDEXS(NPX) in labeled common SETUPL
INDEXW(NPX) in labeled common SETUPL
KOUNT in labeled common SETUPG
KOUNTS in labeled common SETUPL
KOUNTW in labeled common SETUPL
MAXPT(NPX) in labeled common RESLT
MINPT(NPX) in labeled common RESLT
RPTOUT in labeled common UNITS
SEDCOL(NPX) in labeled common MASSL
SEDMSL(NPX) in labeled common MASSL
SSOUT in labeled common UNITS
SYSTYP(60) in labeled common NAME2G
TYPEE(NPX) in labeled common NAME2G
WATVOL(NPX) in labeled common MASSL
Z(18) in labeled common RESULT

IV. USAGE

A. ENTRY POINT: AVEOUT

B. CALLING SEQUENCE: CALL AVEOUT(Y)

C. INPUT ARGUMENTS: Y - steady-state concentration vector for synthetic organic chemical

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

Output concentration variables are computed as the product of the appropriate distribution coefficient (ALPHA) and the total concentration of chemical (Y) in each compartment. Average values are found by summing over compartments followed by division by the number of compartments involved. Concentration maxima and minima are found by simple magnitude testing.

I. IDENTIFICATION

A. TITLE: FLXOUT

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Jan. 1981

II. PURPOSE: FLXOUT analyzes and reports the steady-state fate of synthetic organic chemicals.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

BIOLKL(NPX) in labeled common CHEM1L
BIOPCT in labeled common RESLT
CHEMNA(60) in labeled common NAME1G
CHEMPC in labeled common RESLT
EXPOKL(NPX) in labeled common CHEM1L
EXPPCT in labeled common RESLT
HYDRKL(NPX) in labeled common CHEM1L
INDEXS(NPX) in labeled common SETUPL
KDTIME in labeled common TIMEL
KINOUT in labeled common UNITS
KOUNT in labeled common SETUPG
OXIDKL(NPX) in labeled common CHEM1L
PHOTKL(NPX) in labeled common CHEM1L
RPTOUT in labeled common UNITS
SYSLDL in labeled common MISCL
SYSTYP(60) in labeled common NAME2G
TFACTR in labeled common TIMEL
TFINAL in labeled common TIMEL
TINCR in labeled common TIMEL
VOLKL(NPX) in labeled common CHEM1L
VOLPCT in labeled common RESLT
WATVOL(NPX) in labeled common MASSL
Z(18) in labeled common RESULT

IV. USAGE

A. ENTRY POINT: FLXOUT

B. CALLING SEQUENCE: CALL FLXOUT(Y)

C. INPUT ARGUMENTS: Y - steady-state concentration vector

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

Subroutine FLXOUT analyzes and reports the steady-state fate of synthetic organic chemicals. The information reported for each process includes the mass flux (kg/time) attributable to the process, the percentage of the total load consumed in the process, and a projected (first-order) half-life that would result from each process acting in isolation absent internal transport limitations. The processes are also summed by category (chemical, biological, transport), and a total system half-life is estimated from the total flux. The latter is used to specify a time-frame for the numerical integration routines (RKFINT and STFINT).

The fluxes are computed as the sum over compartments of the product of concentration (Y(J)) and the pseudo-first-order rate constant of each process in the compartment (computed in FIRORD). Halflives are estimated as 0.69 times the resident chemical mass divided by the flux. The appropriate time-frame for reporting results (hours, days, months, or years) is computed from the (estimated) overall system halflife of the chemical. An overall mass balance is struck as the residual loading not accounted for by process fluxes. The fate of the chemical (process fluxes, mass balance, etc.) is written to the output file defined by FORTRAN logical unit RPTOUT.

I. IDENTIFICATION

A. TITLE: DRIVER

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Oct. 1979

D. REVISION: May 1980

II. PURPOSE: dispatching routine for EXAMS' integrators.

III. RESTRICTIONS:

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED:
- FCT
- FDER
- OUTP
- RKFINT
- STFINT

C. COMMON STORAGE:

IFLAG in labeled common TIMEL
KDTIME in labeled common TIMEL
KOUNT in labeled common SETUPG
NPRINT in labeled common TIMEL
RPTOUT in labeled common UNITS
T in labeled common TIMEL
TFINAL in labeled common TIMEL
TINCR in labeled common TIMEL
TPRINT in labeled common TIMEL
TTYOUT in labeled common UNITS

IV. USAGE

A. ENTRY POINT: DRIVER

B. CALLING SEQUENCE: CALL DRIVER(Y)

C. INPUT ARGUMENTS: Y -- steady-state concentration vector

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: Returns with IFLAG = 9 if integrators fail.

V. ALGORITHM OR METHOD

Subroutine DRIVER is primarily a dispatching routine that calls the EXAMS numerical integration subroutines RKFINT and STFINT. DRIVER initially calls RKFINT to integrate the kinetic equations from t = 0.0 to TFINAL. If RKFINT returns with IFLAG=6 (stiff equations), DRIVER calls STFINT to continue the integration from the current value of t to TFINAL. If either integrator returns abnormally (e.g., T.LT.TFINAL), DRIVER checks for the existence of partial results that can be used to calculate the persistence of the chemical (computed in subroutine SUMUP).

The integration routines have been described by Malanchuk, Otis, and Bouver (1980). EXAMS uses both a Runge-Kutta and a Gear's (stiff equation) routine from this publication, including: RKFINT, RKFS; STFINT, STIFF, GINTRP, GEAR, DECOMP; and the user-supplied (i.e., problem-specific) routines FCT, FDER, and OUTP.

Several minor modifications of these routines were implemented to enable their use in EXAMS:

1. For both RKFINT and STFINT:

   a. three parameters (TT, IIFLAG, and TPRINT) were added to the calling sequence in order to return the current values of T, IFLAG, and TOUT to subroutine DRIVER.

   b. a counter (NPRINT in labeled common TIMEL) was added to track the number of calls to OUTP -- this counter is used (in DRIVER) to determine whether a successful partial integration has been executed, i.e., whether sufficient data is available to compute persistence despite failure of the integrators to reach a normal completion.

   c. program STOPs were converted to RETURNs.

2. RKFINT returns immediately to DRIVER if the kinetic equations are "stiff"; DRIVER then invokes STFINT to continue the integration from the current value of T toward TFINAL.

3. In order to control the expense of the job,

   a. counter MAXNFE in RKFS was reduced from 6000 to 3000.

   b. counter NBLFE was added to STFINT; integration is terminated at the expiration of 2 blocks of MAXNFE.

I. IDENTIFICATION

A. TITLE: FCT

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Oct. 1980

II. PURPOSE: FCT evaluates derivatives YP(J) = DY(J)

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

INTINL(NPX,NPX) in labeled common CHEM1L
KOUNT in labeled common SETUPG
TOTKL(NPX) in labeled common CHEM1L

IV. USAGE

A. ENTRY POINT: FCT

B. CALLING SEQUENCE: CALL FCT(TIME,Y,DY)

C. INPUT ARGUMENTS: TIME - independent variable
Y - solution vector at TIME

D. OUTPUT ARGUMENTS: YP - rate of change of Y at TIME

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

FCT computes the rate of change of chemical concentration (Y) in each ecosystem compartment from the relationship:

DY(J)/DT = -TOTKL(J)*Y(J) + (Sum [Y(I)*INTINL(I,J)])

where TOTKL is the first-order loss coefficient and the INTINL are first-order coefficients expressing the effects of internal transport on chemical concentrations.

I. IDENTIFICATION

A. TITLE: FDER

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR,DATE: L.A. Burns, Oct. 1979

D. REVISION: Jul. 1980

II. PURPOSE: FDER computes Jacobian matrix for EXAMS.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

INTINL(NPX,NPX) in labeled common CHEM1L
KOUNT in labeled common SETUPG
TOTKL(NPX) in labeled common CHEM1L

IV. USAGE

A. ENTRY POINT: FDER

B. CALLING SEQUENCE: CALL FDER(TIME,Y,W,YP,DER)

C. INPUT ARGUMENTS: TIME - current value, independent variable
Y - solution vector at TIME
YP - derivatives DY/DT at TIME
DER - dummy subroutine name

D. OUTPUT ARGUMENTS: W - Jacobian matrix

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

The Jacobian matrix for the EXAMS chemical disappearance integration is constant. Subroutine FDER transfers -TOTKL to the diagonal of working matrix W, and loads the remainder of W from matrix INTINL.

I. IDENTIFICATION

A. TITLE: OUTP

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Oct. 1980

II. PURPOSE: OUTP records results of time-trace computations in output files.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

ALPHA(18,NPX) in labeled common PARTIL
AREAG(NPX) in labeled common GEOMT
BIOTOL(NPX) in labeled common MASSL
INDEXS(NPX) in labeled common SETUPL
KINOUT in labeled common UNITS
KOUNT in labeled common SETUPG
KOUNTS in labeled common SETUPL
KOUNTW in labeled common SETUPL
RPTOUT in labeled common UNITS
SEDCOL(NPX) in labeled common MASSL
TFACTR in labeled common TIMEL
WATVOL(NPX) in labeled common MASSL
Z(18) in labeled common RESULT

IV. USAGE

A. ENTRY POINT: OUTP

B. CALLING SEQUENCE: CALL OUTP(TIME,Y,W)

C. INPUT ARGUMENTS: TIME - current value, independent variable
Y - solution vector at TIME
W - 1st derivatives of Y at TIME

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

Subroutine OUTP transforms EXAMS' internal state variable (Y) to the concentration variables used for output, and writes the current values of the independent and dependent variables to the output files defined by FORTRAN logical units RPTOUT and KINOUT.

I. IDENTIFICATION

A. TITLE: SUMUP

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: L.A. Burns, Aug. 1979

D. REVISION: Nov. 1980

II. PURPOSE: SUMUP estimates ecosystem self-cleansing time and writes a summary of all analyses executed by EXAMS.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

BIOPCT in labeled common RESLT
CHEMPC in labeled common RESLT
DOMAX(10) in labeled common RESLT
EXPPCT in labeled common RESLT
IFLAG in labeled common TIMEL
KDTIME in labeled common TIMEL
QSSAV in labeled common RESULT
QTSAV in labeled common RESULT
QWSAV in labeled common RESULT
RPTOUT in labeled common UNITS
SYSLDL in labeled common MISCL
TFACTR in labeled common TIMEL
TFINAL in labeled common TIMEL

VOLPCT in labeled common RESLT
Z(18) in labeled common RESULT

IV. USAGE

A. ENTRY POINT: SUMUP

B. CALLING SEQUENCE: CALL SUMUP

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

Subroutine SUMUP is primarily a data summary routine; it writes a single-page summary of all prior analyses conducted by EXAMS to the output file designated by LUN RPTOUT. Subroutine SUMUP also estimates the persistence of the chemical from the outcome of numerical integration of the equations describing transformation and transport losses. An overall "system self-purification time" is estimated as the weighted mean of five halflives (first-order approximation) for removal of the chemical from the water column and bottom sediments of the ecosystem. These halflives are weighted according to the initial steady-state distribution of the chemical, that is, a rapid loss of chemical from the water column is heavily discounted if 99.9% of the material resides in bottom sediments, and conversely.

APPENDIX B

DOCUMENTATION OF INTERACTIVE USER INTERFACE SUBROUTINES

EXAMS' interactive subroutines are executed as a function of user input -- not in a fixed sequence. The executive routine MAIN calls WHTCMD to determine the intent of the user. After a valid command has been identified, the executive passes control to the subroutine responsible for the desired action.

Utilities Group

The utilities group of subroutines is co-resident with EXAMS' executive routine. Utility routines execute unit operations for the functional subroutines described below.

GETNUM. GETNUM scans the input string and returns the numerical equivalent of the characters encountered.

IHELP. IHELP determines whether either the keyword "HELP," or the keyword "EXIT," is contained in the input string "INPUT."

INREC. INREC reads a single record from logical unit "UNIT." The result is transmitted to the calling program in the variable "INPUT." End-of-file is indicated by "EOF," which is 0 if no end-of-file is encountered and 1 if end-of-file is found. An audit trail is produced, if requested by the user.

IMBED. IMBED locates the first non-blank character in a character string.

LRAIL. LRAIL searches for the last non-blank character proceeding from the end of the string toward the beginning.

MATCH. MATCH tests whether an input string "INPUT" is a member of the table of strings "NAME." There are "NUMB" strings in "NAME," each having a length defined by "LENS."

MATCHC. MATCHC determines where the string "STR2" is imbedded in string "STRING."

SCAN. SCAN examines a character string for specified delimiters and returns the index of the first delimiter encountered.

SHOENV. SHOENV lists the system-defined names from the environmental database on the terminal.

VALUE. VALUE converts a character string to a numerical value. The only acceptable characters are the digits 0, 1, 2, 3, 4, 5, 6, 7, 8, and 9, plus the delimiters -, +, ., E, and D.

Functional Groups

The functional group that decodes the user's input contains a single subroutine, WHTCMD.

WHTCMD. WHTCMD prompts the user for a command, accepts the command and returns to the calling program.

The functional group that executes the STORE and ERASE commands includes subroutines ERASE, PACK, PAKENV, and STORE.

ERASE. ERASE replaces the information stored in the selected record of the chemical or environmental database with null values. Any information in the selected record prior to execution of the ERASE command is destroyed.

PACK. PACK copies the data contained in the labeled COMMONs associated with the descriptions of the chemical, to a single vector. The resulting vector is written to the chemical database. Conversion to a single vector minimizes I/O time.

PAKENV. PAKENV copies data contained in the labeled COMMONs associated with the currently selected environment, to a single vector. The vector is written to the environmental database. Conversion to a single vector minimizes I/O time.

STORE. STORE loads the current environment or chemical into the user database, for permanent storage and later retrieval via the "RECALL" command.

The functional group that executes the CHANGE command includes the subroutines CHANGE and MODIFY.

CHANGE. CHANGE either assigns a value to a variable or transfers the value of a variable to a temporary location.

MODIFY. MODIFY changes variables of the computational model.

The functional group that executes the HELP and DESCRIBE commands includes subroutines DESOUT, DESCRI, and HELP.

DESCRI. DESCRI lists the attributes of a variable, including the data and storage type and the number of row and columns.

DESOUT. DESOUT transmits the attributes of a variable contained in labeled COMMON to the user's terminal.

HELP. HELP provides on-line assistance to the user.

The functional group that executes the TERMINAL command consists of a single subroutine, TERMAL.

TERMAL. TERMAL sets TERMTY to a code that represents the user-specified terminal type.

The functional group that executes the SHOW command includes subroutines CHANGE, HEDSHO, IFIND, LISSTR, PRCHEM, PRENV, PRTPRM, SHOW, STEADY, and USROPT.

CHANGE. CHANGE either assigns a value to a variable or transfers the value of a variable to a temporary location.

HEDSHO. HEDSHO is called by subroutine SHOW to list table headings.

IFIND. IFIND gets the next input token, calls subroutine MATCH to determine whether the token is contained in the table of strings ("NAME"), and returns the table index of the identified token. the parameter "MSG" is used to prompt for more input if the input token is not identified.

LISSTR. LISSTR lists the ecosystem number--name pairs.

PRCHEM. PRCHEM is discussed in Appendix A.

PRENV. PRENV is discussed in Appendix A.

PRTPRM. PRTPRM is called in response to the SHOW <variable name> command and prints the the requested value on the terminal.

SHOW. SHOW implements the SHOW command, and displays any of the following information on the terminal when selected: available compounds and environments, chemical parameters describing the currently selected compound, and environmental parameters of the currently selected environment. In addition, any of the labeled COMMON variables associated with the currently selected compound or environment can be displayed.

STEADY. STEADY is discussed in Appendix A.

USROPT. USROPT lists user-defined compounds and environments.

The functional group that executes the RUN, PRINT, and LIST commands includes the subroutines LIST and RUNIT.

LIST. LIST compiles all or selected portions of the output report file. The file is accessed via FORTRAN unit RPTOUT.

RUNIT. RUNIT is called in response to the run command to ensure that a compound and environment have been selected, that the aqueous solubility is greater than 0.0, and that at least one load has been specified.

The functional group that executes the PLOT command includes subroutines DATOPT, IFIND, PLOTX, PONDAT, PRODAT, SCALE, STAOPT, TYPOPT, VSTR, XBAR, and ZONOPT.

DATOPT. DATOPT identifies the kind of data to be plotted.

IFIND. IFIND gets the next input token, calls subroutine MATCH to determine whether the token is contained in the table of strings ("NAME"), and returns the table index of the identified token. The parameter "MSG" is used to prompt for more input if the input token is not identified.

PLOTX. PLOTX plots the steady-state results on the terminal. It is an interim product and will be replaced with an enhanced version. The current version can be used as a guide for extracting parameters from the output files.

PONDAT. PONDAT retrieves specific records from the plot file. Statistical information about the simulation is collected. These data are available in two different forms: water column, and bottom sediments. Each of the forms has three parts: average, maximum, and minimum.

PRODAT. PRODAT retrieves data from the steady-state output file to be used for plotting profiles.

SCALE. SCALE is the equivalent of routines that are supplied with digital incremental plotters. The routine scans the input data and computes a starting value and a scaling factor. These values are used to scale the input data to ensure that it will fit in the user-defined plotting area.

STAOPT. STAOPT identifies the statistical option to be plotted.

TYPOPT. TYPOPT determines the type of plot requested.

VSTR. VSTR moves the LEN characters stored in the vector "STRING" into the uppermost positions of column "X" of the matrix "AREA." The matrix has MAXY rows.

XBAR. XBAR inscribes a vertical bar on the plotting area, "AREA."

ZONOPT. ZONOPT identifies the zone that is to be plotted.

The functional group that executes the COMPOUND, ENVIRONMENT, and RECALL commands includes subroutine COMPND, ENVIRO, NEWNAM, RECALL, UNPACK, and UNPENV.

COMPND. COMPND allows the user to select a compound or to change the name of the currently selected compound.

ENVIRO. ENVIRO allows the user to select an environment or to change the name of the currently selected environment.

NEWNAM. NEWNAM obtains a user-defined name.

RECALL. RECALL retrieves a selected record from the environmental or chemical database. This routine implements the "RECALL" command.

UNPACK. UNPACK reads a record from the chemical database. This information is then copied to the labeled COMMON variables associated with the descriptions of chemicals. The data are read as a single vector to minimize I/O time.

UNPENV. UNPENV reads the specified environmental record and transfers the information to the variables used to describe the environment.

Action for the AUDIT, STOP, EXIT, and QUIT commands is performed internally by the executive.

After the user-entered RUN command has been validated by the

RUNIT subroutine, the subroutines described in Appendix A are invoked. Subroutine DATAIN is not included in the interactive version of EXAMS.

I. IDENTIFICATION

A. TITLE: CHANGE

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: CHANGE either assigns a value to a variable or transfers the value of a variable to a temporary location.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

All variables in labeled common NAME1G
All variables in labeled common CONTRG
All variables in labeled common PCHEMG
All variables in labeled common IONG
All variables in labeled common PARTG
All variables in labeled common VOLATG
All variables in labeled common DPHOTG
All variables in labeled common HYDROG
All variables in labeled common OXIDG
All variables in labeled common BACTG
All variables in labeled common NAME2G
All variables in labeled common SETUPG
All variables in labeled common SEDMG
All variables in labeled common QUALG
All variables in labeled common PHOG
All variables in labeled common GEOMT
All variables in labeled common CLIMG
All variables in labeled common FLOWG

All variables in labeled common UNITS
All variables in labeled common M23456

IV. USAGE

A. ENTRY POINT: CHANGE

B. CALLING SEQUENCE: CALL CHANGE

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS: None

V. ALGORITHM OR METHOD:

The variables to be changed are organized as a function of the labeled COMMON in which they are defined. A computed GO TO statement using the variable ICOM directs the program flow to the desired location. When the labeled COMMON area is reached, another computed GO TO statement using the variable IVAR directs the program flow to the section of code where the selected variable is changed. The variable RDWR determines whether the variable is to read or changed. If RDWR=0, the variable is set to the quantity provided by the calling program. If RDWR is set to "1," the data are copied to a temporary variable for use by the calling program.

I. IDENTIFICATION

A. TITLE: DATOPT

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: DATOPT identifies the kind of data to be plotted.

III. RESTRICTIONS:

A. MACHINE DEPENDENCY:

Initialization of the vector DATMSG requires 8 characters per data element. This dependency can be overcome by providing a vector that will accomodate 80 characters and by redefining the DATA statement.

B. OTHER ROUTINES REQUIRED: IFIND

C. COMMON STORAGE:

TTYOUT in labeled common UNITS

IV. USAGE

A. ENTRY POINT: DATOPT

B. CALLING SEQUENCE: CALL DATOPT(IDAT)

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS:

IDAT (Scalar, Integer) -- receives the option:

1: Total, mg/L in water column
          mg/kg in benthic sediments

2: Dissolved, mg/L

3: Particulate, sediment-sorbed, mg/kg

4: Biota, biosorbed, ug/g

5: Mass, chemical mass as grams/m2 area

E. ERROR CONDITIONS AND RETURNS:

IDAT is set to -1 if an end-of-file is encountered.

V. ALGORITHM OR METHOD:

Calls subroutine IFIND to determine the type of data requested.

I. IDENTIFICATION

A. TITLE: DESCRI

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: DESCRI lists the attributes of a variable, including the data and storage type and the number of row and columns.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED:
DESOUT
IMBED
INREC
MATCH
SCAN

C. COMMON STORAGE:

INPUT in labeled common INPAR
MODLEN in labeled common INPAR
MODMIN in labeled common INPAR
MODS in labeled common INPAR
NOMOD in labeled common INPAR
START in labeled common INPAR
STOP in labeled common INPAR
TD in labeled common INPAR
TTYIN in labeled common INPAR
TTYOUT in labeled common INPAR
TYPE in labeled common INPAR

IV. USAGE

A. ENTRY POINT: DESCRI

B. CALLING SEQUENCE: CALL DESCRI

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS:

If an end-of-file is encountered, the name of the variable is not identified, or a COMMON name is specified, an error message is printed and control returns to the calling program.

V. ALGORITHM OR METHOD:

The input string, "INPUT," is scanned for the name of a variable. If the input is null, the user is prompted for the name of a variable. Once the name of a variable is found, subroutine MATCH is called to determine the validity of the name. If invalid, an error message is printed and control returns to the calling program. If valid, the full variable name is copied to the vector, "OUT." Subroutine DESOUT is then called to print the attributes at the terminal.

I. IDENTIFICATION

A. TITLE: DESOUT

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: DESOUT lists the attributes of a variable contained in labeled COMMON, at the user's terminal.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

TCOL in labeled common INPAR
TD in labeled common INPAR
TROW in labeled common INPAR
TS in labeled common INPAR

TTYOUT in labeled common INPAR

IV. USAGE

A. ENTRY POINT: DESOUT

B. CALLING SEQUENCE: CALL DESOUT(INDX,NAME,LEN)

C. INPUT ARGUMENTS:

INDX (Scalar, Integer) - holds the table offset that points to the attribute codes held in the TCOL, TD, TROW, and TS vectors.

NAME (Vector, Integer) - holds the name of the variable, one character per element.

LEN (Scalar, Integer) - holds the number of characters in NAME.

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD:

The name of the variable held in NAME and the string "IS A" are copied to the vector "OUTPUT," one character per element. The codes for the data type, that is, REAL, INTEGER, LOGICAL, etc., are held in TD. The codes for storage mode, that is SCALAR, VECTOR, or MATRIC are held in TS. The number of rows is held in TROW, and the number of columns is held in TCOL. INDX is used as an index to retrieve the codes in TD, TCOL, TS, and TROW. The codes for data type, data storage, number of rows and number of columns are converted to characters and copied to OUTPUT. OUTPUT is transmitted to the user's terminal via FORTRAN unit TTYOUT.

I. IDENTIFICATION

A. TITLE: ENVIRO

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: ENVIRO allows the user to select an environment or to change the name of the currently selected environment.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED:

IHELP
IMBED
INREC
MATCH
NEWNAM
SCAN
SHOENV
UNPENV

C. COMMON STORAGE:

DRFLDG(NPX) in labeled common LOADSG
ECOLEN(64) in labeled common INPAR
ECONAM(800) in labeled common INPAR
IENV in labeled common INPAR
IFLLDG(NPX) in labeled common LOADSG
INENVR in labeled common UNITS
INPUT in labeled common INPAR
MINECO(64) in labeled common INPAR
NOECOS in labeled common INPAR
NPSLDG(NPX) in labeled common LOADSG
PCPLDG(NPX) in labeled common LOADSG
START in labeled common INPAR
STOP in labeled common INPAR
STRLDG(NPX) in labeled common LOADSG
SYSTYP(60) in labeled common NAME2G
TTYIN in labeled common UNITS
TTYOUT in labeled common UNITS
TYPE in labeled common INPAR

IV. USAGE

A. ENTRY POINT: ENVIRO

B. CALLING SEQUENCE: CALL ENVIRO

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS:

If errors are detected during the execution of this routine, appropriate messages are printed on the user's terminal before returning to the calling routine.

V. ALGORITHM OR METHOD:

Subroutine ENVIRO is called in response to the the ENVIRONMENT command. The input string "INPUT" is scanned for the keywords "IS" or "NAME IS." If invalid input is encountered, then an error message is printed and control returns immediately to the calling routine. If the input proves to be null, or the input is incomplete, the user is prompted with a message appropriate to the situation. When the keyword "IS" is detected and followed by a valid name of an environment, IENV is set to the database record number that holds the environmental information. The data are read via FORTRAN unit INENVR.

If the keyword "NAME IS" is detected, the name of the environment is changed to that entered by the user.

If the keyword "EXIT" or the keyword "HELP" is detected during the execution of this routine, one of the following occurs:

EXIT - causes an immediate return to the calling routine.

HELP - prints a short message informing the user of possible responses.

I. IDENTIFICATION

A. TITLE: ERASE

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, May 1980

D. REVISIONS: None

II. PURPOSE: ERASE replaces the information stored in the selected record of the chemical or environmental database with null values. Any information that in the selected record prior to the execution of the ERASE command is destroyed.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED:

GETNUM
IHELP
IMBED
INREC
MATCH
SCAN

C. COMMON STORAGE:

INCOMP in labeled common UNITS
INENVR in labeled common UNITS
INPUT in labeled common INPAR
NOCREC in labeled common INPAR
NOECOS in labeled common INPAR
NOEREC in labeled common INPAR
NONAME in labeled common INPAR
START in labeled common INPAR
STOP in labeled common INPAR
TTYIN in labeled common UNITS
TTYOUT in labeled common UNITS
TYPE in labeled common INPAR

IV. USAGE

A. ENTRY POINT: ERASE

B. CALLING SEQUENCE: CALL ERASE

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS:

If the selected record exceeds the range of allowable record numbers established for the user, an error message is printed on the user's terminal.

V. ALGORITHM:

The input string "INPUT" is scanned for the keywords "COMPOUND" or "ENVIRONMENT" to determine which database contains the input record to be erased. GETNUM is called to extract the record number. The record number is tested to ensure that it is in the range of user-defined record numbers. A vector with an appropriate number of blanks and zeroes is written to the selected database. If the "COMPOUND" option was specified, the information is written to the chemical database via FORTRAN unit INCOMP; FORTRAN unit INENVR is used to transmit the information to the environmental database when the "ENVIRONMENT" option is specified.

I. IDENTIFICATION

A. TITLE: GETNUM

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: GETNUM scans the input string and returns the numerical equivalent of the characters encountered.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED:
IMBED
SCAN
VALUE

C. COMMON STORAGE:

INPUT in labeled common INPAR
START in labeled common INPAR
STOP in labeled common INPAR

IV. USAGE

A. ENTRY POINT: GETNUM

B. CALLING SEQUENCE: CALL GETNUM(ERR,RESULT)

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS:

ERR (Scalar, Integer)	is used as an error indicator.
RESULT (Scalar, Real)	receives the converted numerical quantity.

E. ERROR CONDITIONS AND RETURNS:

0: No errors detected
1: Null input
2: Non-numeric character encountered

V. ALGORITHM OR METHOD:

The characters are isolated in the input string "INPUT," and subroutine VALUE is called to convert the characters to a numerical quantity.

I. IDENTIFICATION

A. TITLE: HEDSHO

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: HEDSHO is called by the SHOW subroutine to list table headings.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

KOUNT in labeled common SETUPG
SYSTYP(60) in labeled common NAME2G
TTYOUT in labeled common UNITS
TYPEE(NPX) in labeled common NAME2G

IV. USAGE

A. ENTRY POINT: HEDSHO

B. CALLING SEQUENCE: CALL HEDSHO

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

The names of the currently selected environment and chemical are printed, followed by the compartment type codes (L, H, etc.).

I. IDENTIFICATION

A. TITLE: HELP

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: HELP provides on-line assistance to the user.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED:

DESOUT
INBED
INREC
LRAIL
MATCH
SCAN

C. COMMON STORAGE:

HELP in labeled common INPAR
HELEN (50) in labeled common INPAR
HELPS (300) in labeled common INPAR
INDEF in labeled common UNITS
INHLP in labeled common UNITS
INPUT (80) in labeled common INPAR
MINHLP (50) in labeled common INPAR
MODLEN (120) in labeled common INPAR
MODMIN (120) in labeled common INPAR
MODS (500) in labeled common INPAR
NOHELP in labeled common INPAR
NOMOD in labeled common INPAR
START in labeled common INPAR
STOP in labeled common INPAR
TD (120) in labeled common INPAR
TTYOUT in labeled common UNITS
TYPE in labeled common INPAR

IV. USAGE

A. ENTRY POINT: HELP

B. CALLING SEQUENCE: CALL HELP

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

The input string "INPUT" is scanned for a keyword or the name of a variable in the labeled COMMONs reserved for the chemical and environmental parameters. If no input is encountered, then a list of available keywords is printed on the terminal. If a token is found in the input stream, MATCH is called to determine whether it is contained in the table of keywords. If a match is made, text is read from the file connected to FORTRAN unit INHLP and the text is printed on the terminal. In the event that the MATCH routine fails to identify the token, MATCH is called again with a table of the labeled COMMON variables mentioned above to determine whether assistance was requested for one of them. If a match is made, text is then read via FORTRAN unit INDEF and printed at the terminal. If the match fails, a list of available keywords is printed at the terminal.

I. IDENTIFICATION

A. TITLE: IFIND

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: IFIND gets the next input token, calls subroutine MATCH to determine whether the token is contained in the table of strings (NAME), and returns the table index of the identified token. The parameter "MSG" is used to prompt for more input if the input token is not identified.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: IMBED

INREC
MATCH
SCAN

C. COMMON STORAGE:

INPUT in labeled common INPAR
START in labeled common INPAR
STOP in labeled common INPAR
TTYIN in labeled common UNITS
TTYOUT in labeled common UNITS
TYPE in labeled common INPAR

IV. USAGE

A. ENTRY POINT: IFIND

B. CALLING SEQUENCE:

```
I=IFIND(NUMB,LENS,NAME,MINS,MSG,PROMPT)
```

C. INPUT ARGUMENTS:

NUMB (Scalar) - number of entries in the tables

LENS (Vector) - lengths of "NAME" entries

NAME (Vector) - table of names in successive elements, 1 character per element.

MINS (Vector) - minimum lengths of "NAME" entries required for uniqueness.

MSG (Vector) - holds object-time FORMAT specifications. Used when prompting is requested.

PROMPT (Scalar) - denotes whether or not prompting is required when the user's input is missing or invalid.

D. OUTPUT ARGUMENTS:

Returned as IFIND(NUMB,LENS,NAME,MINS,MSG,PROMPT)

E. ERROR CONDITIONS AND RETURNS:

IFIND = 0 -- if no user input or the input cannot be identified and PROMPT = 1.

IFIND = I -- an index that points to the entry in the table that matched the input provided by the user. I=1, if the first table entry matched the user's input. I=2, for the second table entry, etc.

V. ALGORITHM OR METHOD

The input string "INPUT" is scanned for a token. If a token is found, subroutine MATCH is called to determine whether the token matches any of the entries in the table NAME.

If an invalid or null response is provided when PROMPT is set to 0, the user is asked for more input. When PROMPT is set to 1, control returns immediately to the calling program.

I. IDENTIFICATION

A. TITLE: IHELP

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: IHELP determines whether the keyword "HELP," or the keyword "EXIT," is contained in input string "INPUT."

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: MATCH

C. COMMON STORAGE: None

IV. USAGE

A. ENTRY POINT: IHELP

B. CALLING SEQUENCE: CALL IHELP(IT)

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS:

IT (Scalar, Integer) - is coded as follows:

IT	Description
0	Neither "HELP" nor "EXIT" found
1	"HELP" found
2	"EXIT" found

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

Subroutine MATCH is called to determine whether either HELP or EXIT is present.

I. IDENTIFICATION

A. TITLE: IMBED

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR,DATE: Cline, D. M. Aug 1979

D. REVISIONS: None

II. PURPOSE: IMBED locates the first non-blank character in a character string.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE: None

IV. USAGE

A. ENTRY POINT: IMBED

B. CALLING SEQUENCE: J=IMBED(STRING,ISTRT)

C. INPUT ARGUMENTS: STRING, ISTRT

STRING (Vector)	holds the string to be scanned, one character per element
ISTRT (Scalar)	denotes the position in STRING where the scan is to begin.

D. OUTPUT ARGUMENTS: I = IMBED(STRING,ISTRT)

E. ERROR CONDITIONS AND RETURNS:

The value of IMBED is the index of the first non-blank character found in an 80 character string. If the line contains no non-blank characters, then IMBED is set to 100.

V. ALGORITHM OR METHOD

The string "STRING" is scanned for the first occurrence of a blank or horizontal tab, starting at the position given by index ISTRT, up to its 80th character. The position in the string where the blank occurs is returned in IMBED.

I. IDENTIFICATION

A. TITLE: INREC

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: INREC reads a single record from logical unit UNIT. The result is transmitted to the calling program in the variable "INPUT." End-of-file is indicated by "EOF," which is 0 if no end-of-file is encountered and 1 if end-of-file is found. An AUDIT trail is produced, if requested by the user.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE

AUDIT in labeled common INPAR
INPUT in labeled common INPAR
TTYIN in labeled common UNITS

IV. USAGE

A. ENTRY POINT: INREC

B. CALLING SEQUENCE: CALL INREC(EOF,UNIT)

C. INPUT ARGUMENTS:

UNIT (Scalar, Integer) holds the FORTRAN logical unit number used to read the input record.

D. OUTPUT ARGUMENTS:

EOF (Scalar, Integer) is used as an error indicator.

E. ERROR CONDITIONS AND RETURNS:

EOF -- 0: no end-of-file encountered
EOF -- 1: end-of-file encountered

V. ALGORITHM:

The next record is read from the file accessed via FORTRAN logical unit UNIT and the first 80 characters are stored in INPUT. If AUDIT is equal to 1 and UNIT is equal to TTYIN, the record is echoed to the audit trail file via FORTRAN logical unit AUDOUT.

I. IDENTIFICATION

A. TITLE: LISSTR

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: LISSTR lists the ecosystem number--name pairs.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: PRCHEM

C. COMMON STORAGE:

BATCH in labeled common INPAR
CHEMNA (60) in labeled common NAME2G
POUND in labeled common INPAR
RPTOUT in labeled common UNITS
TTYOUT in labeled common UNITS

IV. USAGE

A. ENTRY POINT: LISSTR

B. CALLING SEQUENCE: CALL LISSTR(NUMB,LENGTH,NAMES,COL)

C. INPUT ARGUMENTS: All integers

NUMB (Scalar) - Number of names of compounds

LENGTH (Scalar) - Vector that holds the lengths of the chemical names

NAMES (Vector) - holds the names of compounds, 1 character per element

COL (Scalar) - flag to determine the action to be taken.

= 1, list the system database chemical names.

= 2, lists the parameters describing

the currently selected compound.

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS:

If COL is outside the valid range of values, an error message is printed at the terminal.

V. ALGORITHM OR METHOD:

The input parameter "COL" is tested to determine what action is to be taken. For COL = 1, the names of chemicals are extracted from the input parameter NAMES and listed on the terminal. The first column is the full name used on output tables and the second column is the abbreviated name. When COL=2, subroutine PRCHEM is called and the parameters decribing the currently selected chemical are listed on the terminal. Before PRCHEM is called, BATCH is set to 1 and the output unit RPTOUT is set to TTYOUT. Upon return from PRCHEM, BATCH and RPTOUT are reset to their original values.

I. IDENTIFICATION

A. TITLE: LIST

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: LIST compiles all or selected portions of the output report file. The file is accessed via FORTRAN unit RPTOUT.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: GETNUM

IMBED
INREC
LRAIL
MATCH
MATCHC
SCAN

C. COMMON STORAGE:

INPUT in labeled common INPAR
RPTOUT in labeled common UNITS
START in labeled common INPAR
STOP in labeled common INPAR
TTYIN in labeled common UNITS
TTYOUT in labeled common UNITS
TYPE in labeled common INPAR

IV. USAGE

A. ENTRY POINT: LIST

B. CALLING SEQUENCE: CALL LIST(OUTUNT,SPOOL)

C. INPUT ARGUMENTS: Both integers

OUTUNT (Scalar) - FORTRAN unit for printing output report.

SPOOL (Scalar) - if 0, output is not spooled
if 1, output is spooled

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS:

An error message is printed when end-of-file is encountered, the entry is out-of-range, or when simulation results are not available for listing.

V. ALGORITHM OR METHOD:

The input string "INPUT" is scanned for a token. If none is present, the user is prompted with the options available and requested to enter his choice. When a choice is made, subroutine MATCH is called to determine the type of request; "ALL," "HELP," or "EXIT." If one of these is found, the appropriate action is performed. If the choice is not recognized, subroutine GETNUM is called to determine whether a numeric argument has been specified. A valid numeric response causes a selected portion of the file to be listed on the terminal. If the response is not recognized or is out-of-range, the user is notified and prompted for more input.

I. IDENTIFICATION

A. TITLE: LRAIL

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: LRAIL searches for the last non-blank character proceeding from the end of the string toward the beginning.

III. RESTRICTIONS

A. MACHINE-DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE: None

IV. USAGE

A. ENTRY POINT: LRAIL

B. CALLING SEQUENCE: L=LRAIL(STRING,LEN)

C. INPUT ARGUMENTS: Both integers:

STRING (Vector) - text to be searched
LEN (Scalar) - search starts in this position

D. OUTPUT ARGUMENTS: L = LRAIL(STRING,LEN)

E. ERROR CONDITIONS AND RETURNS:

The position of the last non-blank character in the character string is returned in LRAIL(STRING,LEN). If no non-blank character is found, then the function sets LRAIL to 1.

V. ALGORITHM OR METHOD

The string "STRING" is scanned from the position given by index LEN to position 1. LRAIL is set to the position in the string where the first non-blank character occurs.

I. IDENTIFICATION

A. TITLE: MATCH

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: MATCH tests whether an input string "INPUT" is a member of the table of strings "NAME." There are "NUMB" strings in "NAME," each having a length defined by "LENS."

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

INPUT in labeled common INPAR
START in labeled common INPAR
STOP in labeled common INPAR

IV. USAGE

A. ENTRY POINT: MATCH

B. CALLING SEQUENCE: M = MATCH(NUMB,LENS,NAME,MINS)

C. INPUT ARGUMENTS: All integers

NUMB (Scalar) - number of table entries

LENS (Vector) - lengths of the NAME entries

NAME (Vector) - table of names in successive elements (one character per element)

MINS (Vector) - minimum lengths of NAME entries required for uniqueness

D. OUTPUT ARGUMENTS: Returned as MATCH(NUMB,LENS,NAME,MINS)

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

This routine determines whether a token in the input string "INPUT" is contained in the table of strings, "NAME." The token begins at position START and ends at position STOP-1. The length is computed as (STOP - START). MATCH is normally set to the index of of the table entry that matched the token. If the token is not identified, MATCH is set to 0.

I. IDENTIFICATION

A. TITLE: MATCHC

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: MATCHC determines where the string "STR2" is imbedded in string "STRING."

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE: None

IV. USAGE

A. ENTRY POINT: MATCHC

B. CALLING SEQUENCE: M = MATCHC(STRING,START,LENGTH,STR2,LEN2)

C. INPUT ARGUMENTS:

STRING (Vector, Integer)	- the primary string
START (Scalar, Integer)	- the search begins at STRING(START)
LENGTH (Scalar, Integer)	- number of characters in STRING to be searched from START
STR2 (Vector, Integer)	- the secondary string
LEN2 (Scalar, Integer)	- length of STR2

D. OUTPUT ARGUMENTS: M = MATCHC(STRING,START,LENGTH,STR2,LEN2)

E. ERROR CONDITIONS AND RETURNS:

If string "STR2" is found in "STRING," then the position in "STRING" where the match begins is returned. Otherwise, strings do not match and a value of zero is returned.

V. ALGORITHM OR METHOD:

The search begins in position START in string, STRING. The strings are compared, character for character, until any two characters that are not equivalent are encountered or the entire LEN2 characters are tested without error.

I. IDENTIFICATION

A. TITLE: MNLN

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE:

MNLN determines the minimum number of characters required to uniquely identify a string among a set of strings of varying lengths.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

TTYOUT in labeled common UNITS

IV. USAGE

A. ENTRY POINT: MNLN

B. CALLING SEQUENCE: CALL MNLN(NUMB,LENS,STRING,MINS)

C. INPUT ARGUMENTS:

NUMB (Scalar, Integer) - number of strings

LENS (Vector, Integer) - length of each string

STRING (Vector, Integer) - contains the strings (one character per element)

D. OUTPUT ARGUMENTS:

MINS (Vector, Integer) - receives the minimum lengths

E. ERROR CONDITIONS AND RETURNS:

If duplicate strings are encountered, a message is printed on the terminal and execution stops immediately.

V. ALGORITHM OR METHOD:

Each string is compared against all other strings in the set to determine the minimum number of characters required to uniquely identify each string.

I. IDENTIFICATION

A. TITLE: MODIFY

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: MODIFY dynamically changes variables of the computational sector of EXAMS (Appendix A).

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED:

CHANGE
INREC
MATCH
MATCHC
SCAN
VALUE

C. COMMON STORAGE:

COMVAR in labeled common INPAR
INPUT in labeled common INPAR
MODLEN in labeled common INPAR
MODMIN in labeled common INPAR
MODS in labeled common INPAR
NOCOM in labeled common INPAR
NOMOD in labeled common INPAR
START in labeled common INPAR
STOP in labeled common INPAR
TCOL in labeled common INPAR
TD in labeled common INPAR
TROW in labeled common INPAR
TS in labeled common INPAR
TTYIN in labeled common UNITS

TTYOUT in labeled common UNITS
TYPE in labeled common INPAR

IV. USAGE

A. ENTRY POINT: MODIFY

B. CALLING SEQUENCE: M=MODIFY(IT)

C. INPUT ARGUMENTS:

IT (Scalar, Integer) - used as a dummy argument to satisfy the requirements of a FUNCTION definition.

D. OUTPUT ARGUMENTS:

I=MODIFY(IT)

E. ERROR CONDITIONS AND RETURNS:

ERROR CODE		CONDITION FOUND
-3	-----	COMMON group not found
-2	-----	Invalid name
-1	-----	End-of-file
0	-----	O.K.
+1	-----	Null input
+2	-----	Imbedded blank, system error
+3	-----	COMMON name specified
+4	-----	Only one argument allowed for vectors
+5	-----	No "TO"
+6	-----	Subscript out-of-range
+7	-----	scalars cannot have arguments

V. ALGORITHM OR METHOD

The name of the variable is isolated from the input string "INPUT," and subroutine MATCH is used to identify the variable. If defined, subscripts are decoded. The value to be assigned to the selected variable is isolated and converted to a numerical value via the function VALUE.

I. IDENTIFICATION

A. TITLE: NEWNAM

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: NEWNAM obtains a user-defined name.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: IMBED
INREC

C. COMMON STORAGE:

CHEMNA in labeled common INPAR
INPUT in labeled common INPAR
START in labeled common INPAR
SYSTYP in labeled common NAME2G
TTYIN in labeled common UNITS
TTYOUT in labeled common UNITS

IV. USAGE

A. ENTRY POINT: NEWNAM

B. CALLING SEQUENCE: CALL NEWNAM (IT)

C. INPUT ARGUMENTS:

IT (Scalar, Integer) - 0: replace the name of the currently selected compound

1: replace the name of the currently selected environment

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD:

The name is isolated from the input string "INPUT" and stored in CHEMNA if IT=0 or in SYSTYP if IT=1.

I. IDENTIFICATION

A. TITLE: PACK

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: PACK copies the data contained in the labeled COMMONs associated with the descriptions of the chemical to a single vector. The resulting vector is written to the chemical database. Using a single vector minimizes I/O time.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

All variables in labeled common NAME1G
All variables in labeled common CONTRG
All variables in labeled common PCHEMG
All variables in labeled common IONG
All variables in labeled common PARTG
All variables in labeled common VOLATG
All variables in labeled common DPHOTG
All variables in labeled common HYDROG
All variables in labeled common OXIDG
All variables in labeled common BACTG

IV. USAGE

A. ENTRY POINT: PACK

B. CALLING SEQUENCE: CALL PACK(RECORD,UNIT)

C. INPUT ARGUMENTS:

RECORD(Scalar, Integer) - holds record number to be written

UNIT(Scalar, Integer) - holds the FORTRAN unit number that is connected to the chemical database.

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

The labeled COMMON variables are copied into a single vector. The resulting vector is written to the chemical database via FORTRAN unit UNIT.

I. IDENTIFICATION

A. TITLE: PAKENV

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: PAKENV copies data contained in the labeled COMMON associated with the currently selected environment into a single vector. The vector is written to the environmental database. Use of a single vector minimizes I/O time.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

All variables in labeled common NAME2G
All variables in labeled common SETUPG
All variables in labeled common SEDMG
All variables in labeled common QUALG
All variables in labeled common PHOG
All variables in labeled common GEOMT
All variables in labeled common CLIMG
All variables in labeled common FLOWG

IV. USAGE

A. ENTRY POINT: PAKENV

B. CALLING SEQUENCE: CALL PAKENV(RECORD,UNIT)

C. INPUT ARGUMENTS:

RECORD (Scalar, Integer)	holds number of record to be written
UNIT (Scalar, Integer)	holds the FORTRAN unit number connected to the environmental database

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD:

The labeled COMMON variables are copied into a single vector. The resulting vector is written to the to the requested file via FORTRAN unit "UNIT."

I. IDENTIFICATION

A. TITLE: PLOTX

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: PLOTX plots the steady-state results on the terminal. It is an interim product and will be replaced with an enhanced version. This version can be used as a guide for extracting parameters from the output files.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED:

DATOPT
PONDAT
PRODAT
SCALE
STAOPT
TYPOPT
VSTR
XBAR
ZONOPT

C. COMMON STORAGE:

SSOUT in labeled common UNITS
TTYOUT in labeled common UNITS

IV. USAGE

A. ENTRY POINT: PLOTX

B. CALLING SEQUENCE: CALL PLOTX

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

The plot is created in the matrix "AREA" which has MAXY rows and 61 columns. MAXY is presently set to 21 so that the plot can be accommodated on a DEC VT52/VT55 terminal. After "AREA" has been blanked, the remainder of the plotting options are determined. IOPT is set to 1 for point plots and to 2 for profile plots. The concentration type is coded in IDAT:

IDAT	Concentration type
1	Total
2	Dissolved
3	Particulate
4	Biota
5	Mass

If point plots are selected, the statistical type is determined and coded in IVAL.

IVAL	Statistic
1	Maximum
2	Minimum
3	Average

Data to be plotted are collected via subroutine PONDAT and subsequently plotted. If profile plots are selected, the zone type is determined and coded in IZON.

IZON	Zone
1	Water column
2	Bottom sediments

Data to be plotted are collected via subroutine PRODAT and subsequently plotted. The online assistance (HELP) utility provides a fuller explanation of the plotting options, including concentration units. The tutorial also provide examples of usage.

I. IDENTIFICATION

A. TITLE: PONDAT

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: PONDAT retrieves specific records from the plot file. Statistical information about the simulation is collected. These data are available in two different forms: water column, and bottom sediments. Each of the forms has three parts: average, maximum, and minimum.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

TTYOUT in labeled common UNITS
SSOUT in labeled common UNITS

IV. USAGE

A. ENTRY POINT: PONDAT

B. CALLING SEQUENCE: CALL PONDAT(EOF,WATBOT,NOTE,Y,IVAL)

C. INPUT ARGUMENTS:

IVAL (Scalar, Integer)	denotes the statistical type to be plotted.
WATBOT (Scalar, Integer)	holds selection code: 1: water column, 2: bottom sediments

D. OUTPUT ARGUMENTS:

NOTE (Vector, Integer) - the compartment numbers

Y (Real, Vector) - contains the requested data

EOF (Scalar, Integer) - end-of-file indicator
0 -- no eof,
1 -- eof

E. ERROR CONDITIONS AND RETURNS:

See EOF above

V. ALGORITHM OR METHOD

Records are read via FORTRAN unit SSOUT until the second occurrence of an asterisk is found in the second element of a record. Information for the water column precedes the bottom sediment data in the file. Records are read and the selected data and compartment number are transferred to the Y and NOTE variables.

I. IDENTIFICATION

A. TITLE: PRODAT

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: PRODAT retrieves data from the steady-state output file to be used for plotting profiles.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

SSOUT in labeled common UNITS

IV. USAGE

A. ENTRY POINT: PRODAT

B. CALLING SEQUENCE:

```
CALL PRODAT(EOF,Y1,Y2,N1,N2,NOTE11,NOTE12,NOTE21,NOTE22,IDAT)
```

C. INPUT ARGUMENTS:

EOF (Scalar, Integer)	- end-of-file indicator: 0 -- no eof, 1 -- eof
IDAT (Scalar, Integer)	denotes the concentration types to be plotted

D. OUTPUT ARGUMENTS:

Y1 (Vector, Real)	-	the water column data
Y2 (Vector, Real)	-	the sediment data
N1 (Scalar, Integer)	-	number of water compartments
N2 (Scalar, Integer)	-	number of sediment compartments
NOTE11 (Vector, Integer)	-	the water column compartment number
NOTE12 (Vector, Integer)	-	the water column compartment type
NOTE21 (Vector, Integer)	-	the sediment compartment number
NOTE22 (Vector, Integer)	-	the sediment compartment type

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD:

The file accessed via FORTRAN unit SSOUT contains the steady-state water column and sediment concentrations. The water column records precede the sediment records and are marked by an asterisk in the second element of the ending record. This record contains no useful output data; it is used only as a flag to indicate the end of the water column or sediment data. IDAT is used to compute the subscript of the required concentration type.

I. IDENTIFICATION

A. TITLE: PRTPRM

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: PRTPRM is called in response to the SHOW <variable name> command and prints the the requested value on the terminal.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED:

- CHANGE
- MATCH
- SCAN
- VALUE

C. COMMON STORAGE:

COMVAR in labeled common INPAR
INPUT in labeled common INPAR
MODLEN in labeled common INPAR
MODMIN in labeled common INPAR
MODS in labeled common INPAR
NOCOM in labeled common INPAR
NOMOD in labeled common INPAR
START in labeled common INPAR
STOP in labeled common INPAR
TCOL in labeled common INPAR
TD in labeled common INPAR
TROW in labeled common INPAR
TS in labeled common INPAR
TTYOUT in labeled common UNITS
TYPE in labeled common INPAR

IV. USAGE

A. ENTRY POINT: PRTPRM

B. CALLING SEQUENCE: CALL PRTPRM(IT)

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS:

IT (Scalar, Integer) returns the condition code.

E. ERROR CONDITIONS AND RETURNS:

IT	Condition Code
-3	* COMMON group not found
-2	* name not identified
-1	* E-O-F (End of file)
0	* O. K.
+1	* E-O-L for argument 1
+2	* E-O-L for argument 2
+3	* argument out-of-range
+4	* null input
+5	* wild card specified
+6	* COMMON name specified
+7	* scalar name with dimensions specified
+8	* vector name with more than one dimension

V. ALGORITHM OR METHOD

The name of the variable is extracted from the input string "INPUT" and MATCH is called to determine whether it is a valid name. In the event that the input is not identified or null, control returns to the calling program. When a valid name of a variable encountered, its current value is fetched and an object time FORMAT statement is invoked to transmit the name and its value to the terminal.

I. IDENTIFICATION

A. TITLE: RECALL

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, May 1980

D. REVISIONS: None

II. PURPOSE: RECALL retrieves a selected record from the environmental or chemical database. This routine implements the "RECALL" command.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED:

- GETNUM
- IHELP
- IMBED
- INREC
- MATCH
- SCAN
- UNPACK
- UNPENV

C. COMMON STORAGE:

CHEMNA in labeled common NAME1G
DRFLDG in labeled common LOADSG
IENV in labeled common INPAR
IFFLDG in labeled common LOADSG
INCOMP in labeled common UNITS
INENVR in labeled common UNITS
INPUT in labeled common INPAR
NOCREC in labeled common INPAR
NOECOS in labeled common INPAR
NOEREC in labeled common INPAR
NONAME in labeled common INPAR
NPSLDG in labeled common LOADSG
PCPLDG in labeled common LOADSG
POUND in labeled common INPAR
START in labeled common INPAR
STOP in labeled common INPAR
STRLDG in labeled common LOADSG
SYSTYP in labeled common NAME2G
TTYIN in labeled common UNITS
TTYOUT in labeled common UNITS
TYPE in labeled common INPAR

IV. USAGE

A. ENTRY POINT: RECALL

B. CALLING SEQUENCE: CALL RECALL

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM:

The input string "INPUT" is scanned for the keywords

"COMPOUND" or "ENVIRONMENT" to determine which database contains the input record. GETNUM is called to extract the number of the record to be read. If the "COMPOUND" option was specified, subroutine UNPACK reads the selected record via FORTRAN unit INCOMP, and transfers the information to the parameters used to describe chemicals. If the "ENVIRONMENT" option was specified, subroutine UNPENV reads the selected records via FORTRAN unit INENVR, and transfers the information to the parameters used to describe environments. If missing input is encountered, or invalid information is detected, the user is prompted for additional input, or messages describing the error are printed on the terminal.

I. IDENTIFICATION

A. TITLE: RUNIT

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, May 1980

D. REVISIONS: None

II. PURPOSE: RUNIT is called in response to the RUN command to ensure that a compound and an environment have been selected, that the aqueous solubility is greater than 0.0, and that at least one load has been specified.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

DRFLDG in labeled common LOADSG
IENV in labeled common INPAR
IFFLDG in labeled common LOADSG
KOUNT in labeled common SETUPG
NPSLDG in labeled common LOADSG
PCPLDG in labeled common LOADSG

POUND in labeled common INPAR
SOLG in labeled common PCHEMG
STRLDG in labeled common LOADSG
TTYOUT in labeled common UNITS

IV. USAGE

A. ENTRY POINT: RUNIT

B. CALLING SEQUENCE: CALL RUNIT(IRUN)

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS:

IRUN (Scalar, Integer)	receives the test status: 0 -- one of the tests failed 1 -- all tests passed

E. ERROR CONDITIONS AND RETURNS:

Messages are printed on the terminal if a test failed.

V. ALGORITHM OR METHOD:

The parameters "POUND," "IENV," "SOLG(1)," and the summation of all variables contained in the labeled COMMON LOADSG, are tested to ensure that they all exceed 0.0.

I. IDENTIFICATION

A. TITLE: SCALE

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, April 1981

D. REVISIONS: None

II. PURPOSE: SCALE is the equivalent of routines supplied with digital incremental plotters. The routine scans the input data, and computes a starting value and a scaling factor.

These values are used to scale the input data to assure that it will fit in the user defined plotting area.

III. RESTRICTIONS:

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: SCALE2 (Lewart 1971)

C. COMMON STORAGE: None

IV. USAGE

A. ENTRY POINT: SCALE

B. CALLING SEQUENCE: CALL SCALE(ARRAY,AXLEN,NPTS,INC)

C. INPUT ARGUMENTS:

ARRAY (Vector, Real)	- values to be scaled
AXLEN (Scalar, Real)	- length of the plotting area in inches
NPTS (Scalar, Integer)	- number of values to be scaled
INC (Scalar, Integer)	- not used, but required for compatibility

D. OUTPUT ARGUMENTS:

The NPTS+1 element of the input vector contains the starting value. The NPTS+2 element of the input vector contains the scaling value.

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD:

Lewart, C. 1971. Algorithms SCALE1, SCALE2, and SCALE3 for determination of scales on computer generated plots. Algorithm 463 In: Collected Algorithmns from ACM, Vol. II. Association for Computing Machinery, Inc., New York, New York.

I. IDENTIFICATION

A. TITLE: SCAN

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: SCAN examines a character string for specified delimiters and returns the index of the first delimiter encountered.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE: None

IV. USAGE

A. ENTRY POINT: SCAN

B. CALLING SEQUENCE:

```
CALL SCAN (STRING,START,STOP,TYPE,DELIM,NDELIM)
```

C. INPUT ARGUMENTS:

STRING (Vector, Integer)	- input string
START (Scalar, Integer)	- the index of the first character to be scanned
DELIM (Vector, Integer)	- delimiters
NDELIM (Scalar, Integer)	- number of entries in DELIM

D. OUTPUT ARGUMENTS:

STOP (Scalar, Integer) - index of delimiter found

TYPE (Scalar, Integer) - type of delimiter

E. ERROR CONDITIONS AND RETURNS:

If start is greater than 80, or no delimiter is found, or null line, then TYPE is set to 100 and returned.

V. ALGORITHM OR METHOD:

Each character in "STRING" is compared with each of the characters stored in "DELIM;" if a match is made, the position of the character is returned in "STOP" and "TYPE" is set to the index of the matching character in "DELIM." If a match is not made, the scan continues until a match is made or column 80 is exceeded. This condition causes "TYPE" to be set to 100 and control is returned to the calling program.

I. IDENTIFICATION

A. TITLE: SHOENV

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: SHOENV lists the system-defined names from the environmental database at the terminal.

III. RESTRICTIONS:

A. MACHINE-DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

ECOLEN in labeled common INPAR
ECONAM in labeled common INPAR
NOECOS in labeled common INPAR
TTYOUT in labeled common INPAR

IV. USAGE

A. ENTRY POINT: SHOENV

B. CALLING SEQUENCE: CALL SHOENV

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

V. ALGORITHM OR METHOD:

The names of environments are extracted from the vector "ECONAM," one character per element. The vector "ECOLEN" holds the length of each of the names, and "NOECOS" denotes the number of names available.

I. IDENTIFICATION

A. TITLE: SHOW

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: SHOW implements the SHOW command, and displays information on the terminal when one of the following options is selected:

Keyword	Function listed
COMPOUNDS	- names of chemicals
CHEMISTRY	- chemical parameters describing the currently selected compound
ENVIRONMENTS	- names of environments
USER	- names of user-defined compounds and environments, requires an additional qualifier on COMPOUND or ENVIRONMENT

For the currently selected environment,

GEOMETRY - system geometry
ADVECTION - advective interconnections
TURBULANCE - turbulent interconnections
QUALITY - water quality parameters
GLOBAL - global parameters
LOADS - chemical loadings by system element

In addition, any of the labeled COMMON variables associated with the currently selected chemical or environment may be displayed.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED:

HEDSHO
IFIND
INREC
LISSTR
USROPT
PRENV
PRTPRM
SHOENV
STEADY

C. COMMON STORAGE:

BATCH in labeled common INPAR
IENV in labeled common INPAR
INPUT in labeled common INPAR
MODLEN in labeled common INPAR
MODS in labeled common INPAR
NAMLEN in labeled common INPAR
NOMOD in labeled common INPAR
NONAME in labeled common INPAR
TTYOUT in labeled common UNITS

All variables in labeled common NAME1G
All variables in labeled common CONTRG
All variables in labeled common PCHEMG
All variables in labeled common IONG
All variables in labeled common PARTG
All variables in labeled common VOLATG
All variables in labeled common DPHOTG
All variables in labeled common HYDROG
All variables in labeled common OXIDG
All variables in labeled common BACTG
All variables in labeled common NAME2G

All variables in labeled common SETUPG
All variables in labeled common SEDMG
All variables in labeled common QUALG
All variables in labeled common PHOG
All variables in labeled common GEOMT
All variables in labeled common CLIMG
All variables in labeled common FLOWG
All variables in labeled common LOADS

IV. USAGE

A. ENTRY POINT: SHOW

B. CALLING SEQUENCE: CALL SHOW

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS:

Errors are detected and appropriate messages are printed on the terminal.

V. ALGORITHM OR METHOD:

Subroutine IFIND is called to determine whether one of the options in the keyword table "SHONAM" has been entered. If so, the requested information is printed. If a keyword is not identified, the input is assumed to be a variable name and subroutine PRTPRM is called to identify and list its current value. If no input is received, a list of options is printed on the terminal and the user is requested to enter his choice. In the event that an error is encountered, an appropriate error message is printed and control is returned to the calling program.

I. IDENTIFICATION

A. TITLE: STAOPT

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISION: None

II. PURPOSE: STAOPT identifies the statistical option to be plotted.

III. RESTRICTIONS:

A. MACHINE DEPENDENCY:

Initialization of the vector DATMSG requires 8 characters per data element. This dependency can be overcome by providing a vector that will accomodate 80 characters and by redefining the DATA statement.

B. OTHER ROUTINES REQUIRED: IFIND

C. COMMON STORAGE:

TTYOUT in labeled common UNITS

IV. USAGE

A. ENTRY POINT: STAOPT

B. CALLING SEQUENCE: CALL STAOPT(IVAL)

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS:

IVAL (Scalar, Integer) receives the statistical code:

1 -- maximum
2 -- minimum
3 -- average

E. ERROR CONDITIONS AND RETURNS:

IVAL is set to -1 if an end-of-file is encountered.

V. ALGORITHM OR METHOD:

Calls subroutine IFIND to identify the statistical option requested.

I. IDENTIFICATION

A. TITLE: STORE

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, May, 1980

D. REVISIONS: None

II. PURPOSE: STORE transfers the current set of environmental or chemical descriptors into the user data base for long-term storage and subsequent retrieval via the "RECALL" command.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED:

GETNUM
IHELP
IMBED
INREC
MATCH
PACK
PAKENV
SCAN

C. COMMON STORAGE:

CHEMNA in labeled common NAME1G
INCOMP in labeled common UNITS
INENVR in labeled common UNITS
INPUT in labeled common INPAR
NOCREC in labeled common INPAR
NOECOS in labeled common INPAR
NOEREC in labeled common INPAR
NONAME in labeled common INPAR
START in labeled common INPAR
STOP in labeled common INPAR
SYSTYP in labeled common NAME2G
TTYIN in labeled common UNITS
TTYOUT in labeled common UNITS
TYPE in labeled common INPAR

IV. USAGE

A. ENTRY POINT: STORE

B. CALLING SEQUENCE: CALL STORE

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

V. ALGORITHM OR METHOD:

The input string "INPUT" is scanned for the keywords "COMPOUND" or "ENVIRONMENT" to select the database to use when writing the output record. The record number used in the write operation is contained in the input string, and subroutine GETNUM is used to obtain this quantity. If the "COMPOUND" option was specified, information describing the currently selected chemical is passed to subroutine PACK for writing to the chemical database via FORTRAN unit INCOMP. If the "ENVIRONMENT" option was specified, information describing the currently selected environment is passed to subroutine PAKENV, which writes to the environmental database via FORTRAN unit INENVR. If input is missing or invalid information is detected, the user is prompted for additional input or appropriate error messages are printed on the terminal.

I. IDENTIFICATION

A. TITLE: TERMAL

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: Jan., 1981

II. PURPOSE: TERMAL sets TERMTY to a code that represents the user specified terminal type.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: IREC

MATCH
SCAN

C. COMMON STORAGE:

INPUT in labeled common INPAR
START in labeled common INPAR
STOP in labeled common INPAR
TERMTY in labeled common INPAR
TTYIN in labeled common UNITS
TTYOUT in labeled common UNITS
TYPE in labeled common INPAR

IV. USAGE

A. ENTRY POINT: TERMAL

B. CALLING SEQUENCE: CALL TERMAL

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD:

The input string "INPUT" is scanned for a terminal type. If a token is found, subroutine MATCH is called to determine its validity. If the input string is absent or incomplete, the user is prompted for additional input before MATCH is called. When a valid terminal type is found, TERMTY is set as follows:

TERMTY VALUE	TERMINAL TYPE
1	DEC VT55
2	Tektronix 4010 series
3	TTY compatible

Any other response will leave TERMTY unchanged.

I. IDENTIFICATION

A. TITLE: TYPOPT

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR,DATE: D. Cline, Aug. 1979

D. REVISION: None

II. PURPOSE: TYPOPT determines the type of plot requested.

III. RESTRICTIONS:

A. MACHINE DEPENDENCY:

Initialization of the vector DATMSG requires 8 characters per data element. This dependency can be overcome by providing a vector that will accomodate 80 characters and by redefining the DATA statement.

B. OTHER ROUTINES REQUIRED: IFIND

C. COMMON STORAGE:

TTYOUT in labeled common UNITS

IV. USAGE

A. ENTRY POINT: TYPOPT

B. CALLING SEQUENCE: CALL TYPOPT(ITYP,IOPT)

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS:

ITYP (Scalar, Integer) used as follows:

ITYP	Function
-1	End-of-file encountered
4	User selected, "EXIT"

Any other value indicates an error free return.

IOPT (Scalar, Integer) -- 1: Point plots selected
2: Profile plots selected

E. ERROR CONDITIONS AND RETURNS:

ITYP is used as an error flag as described above.

V. ALGORITHM OR METHOD:

Subroutine IFIND determines the type of plot requested is point or profile.

I. IDENTIFICATION

A. TITLE: UNPACK

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE:

UNPACK reads a record from the chemical database. This information is then copied to the labeled COMMON variables associated with the chemical descriptions. The data are read as a single vector to minimize I/O time.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

All variables in labeled common NAME1G
All variables in labeled common CONTRG
All variables in labeled common PCHEMG
All variables in labeled common IONG
All variables in labeled common PARTG
All variables in labeled common VOLATG
All variables in labeled common DPHOTG
All variables in labeled common HYDROG
All variables in labeled common OXIDG

All variables in labeled common BACTG

IV. USAGE

A. ENTRY POINT: UNPACK

B. CALLING SEQUENCE: CALL UNPACK(RECORD,UNIT)

C. INPUT ARGUMENTS:

RECORD (Scalar, Integer)	holds record number to be read.
UNIT (Scalar, Integer)	holds the FORTRAN unit number that is connected to the chemical database.

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD

Information is read as a single vector from the chemical database via FORTRAN unit UNIT. The results are copied to the labeled COMMON variables used to decribe chemicals.

I. IDENTIFICATION

A. TITLE: UNPENV

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: UNPENV reads the specified environmental record and transfers the information to the variables used to describe the environment.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

All variables in labeled common NAME2G
All variables in labeled common SETUPG
All variables in labeled common SEDMG
All variables in labeled common QUALG
All variables in labeled common PHOG
All variables in labeled common GEOMT
All variables in labeled common CLIMG
All variables in labeled common FLOWG

IV. USAGE

A. ENTRY POINT: UNPENV

B. CALLING SEQUENCE: CALL UNPENV(RECORD,UNIT)

C. INPUT ARGUMENTS:

RECORD (Scalar, Integer)	holds record number to be read.
UNIT (Scalar, Integer)	holds the FORTRAN unit number that is connected to the environmental database.

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD:

The environmental information contained in record "RECORD" is read into a single vector via FORTRAN unit UNIT. The information is then copied from the vector to the appropriate labeled COMMON variables used to describe the environment. A single vector is used to minimize I/O time.

I. IDENTIFICATION

A. TITLE: USROPT

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, May 1980

D. REVISIONS: None

II. PURPOSE: USROPT lists user-defined chemicals and environments.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE:

INCOMP in labeled common UNITS
INENVR in labeled common UNITS
TTYOUT in labeled common UNITS

IV. USAGE

A. ENTRY POINT: USROPT

B. CALLING SEQUENCE: CALL USROPT(WHICH)

C. INPUT ARGUMENTS:

WHICH (Scalar, Integer) - 1, select compounds
                          2, select environments

D. OUTPUT ARGUMENTS: None

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD:

The starting record number in the selected database is computed for the value of WHICH. Then, as each record is read, the name of the chemical or environment, as appropriate, is tested to determine whether it is all blank. If not, the record number and the name are printed on the terminal. In the event that all records are blank for a given database, a message to that effect is printed.

I. IDENTIFICATION

A. TITLE: VALUE

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: Cline, D. M. Aug. 1979

D. REVISIONS: None

II. PURPOSE: VALUE converts a character string to a numerical value. The only acceptable characters are the digits 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, plus the delimiters -, +, ., E, and D.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE: None

IV. USAGE

A. ENTRY POINT: VALUE

B. CALLING SEQUENCE: V = VALUE(DIGIT,LEN)

C. INPUT ARGUMENTS:

DIGIT (Vector, Integer) - characters to be converted

LENGTH (Scalar, Integer) - number of characters in DIGIT

D. OUTPUT ARGUMENTS: Returned as VALUE(DIGIT,LENGTH)

E. ERROR CONDITIONS AND RETURNS:

If a non-numeric character is encountered, VALUE is set to

-0.123456E38.

V. ALGORITHM OR METHOD

Each character is converted to its numerical equivalent and then multiplied by a power of ten, dependent upon its position relative to an existing or implied decimal point. Other characters such as, +, -, E and D are handled in an appropriate fashion.

I. IDENTIFICATION

A. TITLE: VSTR

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: VSTR moves the LEN characters stored in the vector "STRING" into the upper-most positions of column "X" of the matrix "AREA." The matrix has MAXY rows.

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE: None

IV. USAGE

A. ENTRY POINT: VSTR

B. CALLING SEQUENCE: CALL VSTR(X,LEN,MAXY,AREA,STRING)

C. INPUT ARGUMENTS: All integers

X (Scalar)	denotes the column of matrix "AREA"

	that is to receive the data.
LEN (Scalar)	denotes the number of characters to be copied to the matrix.
STRING (Vector)	holds the characters to be transferred to the matrix, 1 character per element.
MAXY (Scalar)	denotes the number of rows in the matrix.

D. OUTPUT ARGUMENTS:

AREA (Matrix) is the matrix that receives the characters.

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD:

The offset for upper-most justification is computed as: (Y1 = MAXY - LEN - 1). The characters are moved to column X from "STRING," one character at a time.

I. IDENTIFICATION

A. TITLE: WHTCMD

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: WHTCMD prompts the user for a command, accepts the command and returns to the calling program.

III. RESTRICTIONS:

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: IMBED
INREC
MATCH

C. COMMON STORAGE:

CMDLEN in labeled common INPAR
INPUT in labeled common INPAR
MINCMD in labeled common INPAR
NCMDS in labeled common INPAR
PRICMD in labeled common INPAR
START in labeled common INPAR
STOP in labeled common INPAR
TTYIN in labeled common UNITS
TTYOUT in labeled common UNITS
TYPE in labeled common INPAR

IV. USAGE

A. ENTRY POINT: WHTCMD

B. CALLING SEQUENCE: CALL WHTCMD(CMD)

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS:

CMD (Scalar, Integer) - index of the command to be executed

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD:

The input string "INPUT" is scanned until a token is detected, or until the end of the string is encountered. If a token is found, subroutine MATCH is called to determine whether a valid command has been entered. A valid entry causes CMD to be set to an index that represents this command. If the token is not a valid command, then the user is prompted for additional input.

I. IDENTIFICATION

A. TITLE: XBAR

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR, DATE: D. Cline, Aug. 1979

D. REVISIONS: None

II. PURPOSE: XBAR inscribes a vertical bar on the plotting area, "AREA."

III. RESTRICTIONS

A. MACHINE DEPENDENCY: None

B. OTHER ROUTINES REQUIRED: None

C. COMMON STORAGE: None

IV. USAGE

A. ENTRY POINT: XBAR

B. CALLING SEQUENCE:

```
CALL XBAR(X,HGT,WIDTH,MAXY,AREA,NOTE,NOTE1)
```

C. INPUT ARGUMENTS:

X (Scalar, Integer) - mid-point of the bar on the horizontal axis

HGT (Scalar, Integer) - magnitude of bar, in print lines

WIDTH (Scalar, Integer) - width, in print positions

MAXY (Scalar, Integer) - maximum number of print lines in the plotting area

NOTE (Scalar, Integer) - character used to form the left and right vertical lines of the bar

NOTE1 (Scalar, Integer) - character used to form the top line of the bar

D. OUTPUT ARGUMENTS:

AREA (Matrix, Integer) - the plotting area of size

MAXY by 61 used as print
image buffer.

E. ERROR CONDITIONS AND RETURNS: None

V. ALGORITHM OR METHOD:

The characters are transferred to the plotting matrix, "AREA," one character per element.

I. IDENTIFICATION

A. TITLE: ZONOPT

B. SOURCE LANGUAGE: FORTRAN IV

C. AUTHOR,DATE: D. Cline, Aug. 1979

D. REVISION: None

II. PURPOSE: ZONOPT identifies the zone to be plotted.

III. RESTRICTIONS:

A. MACHINE DEPENDENCY:

Initialization of the vector DATMSG requires 8 characters per data element. This dependency can be overcome by providing a vector that will accommodate 80 characters and by redefining the DATA statement.

B. OTHER ROUTINES REQUIRED: IFIND

C. COMMON STORAGE:

TTYOUT in labeled common UNITS

IV. USAGE

A. ENTRY POINT: ZONOPT

B. CALLING SEQUENCE: CALL ZONOPT(IZON)

C. INPUT ARGUMENTS: None

D. OUTPUT ARGUMENTS:

IZON (Scalar, Integer) - receives the zone code:

1: water column
2: bottom sediments

E. ERROR CONDITIONS AND RETURNS:

IZON is set to -1 if an end-of-file is encountered.

V. ALGORITHM OR METHOD:

Subroutine IFIND is called to identify the zone option requested.

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